



STIC Search Report

EIC 1700

STIC Database Tracking Number: 195465

TO: Rei-Tsang Shiao
Location: rem/5A10/5C18
Art Unit : 1626
July 24, 2006

Case Serial Number: 10/813822

From: Usha Shrestha
Location: EIC 1700
REMSEN 4B28
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Search Notes

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Scientific and Technical Information Center

SEARCH REQUEST FORM

Requester's Full Name: Robert (Rita) Shiao Examiner #: 79521 Date: 7/13/26
Art Unit: 1026 Phone Number: 2-0707 Serial Number: 19813,822
Location (Bldg/Room#): REM (Mailbox #): 5A10 Results Format Preferred (circle): PAPER DISK
*****15C/8*****

To ensure an efficient and quality search, please attach a copy of the cover sheet, claims, and abstract or fill out the following:

Title of Invention: Alkoxymine derived from Me
Inventors (please provide full names): Couturier et al.

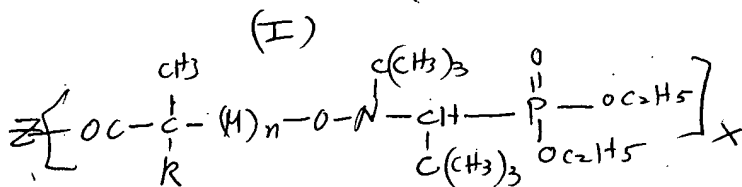
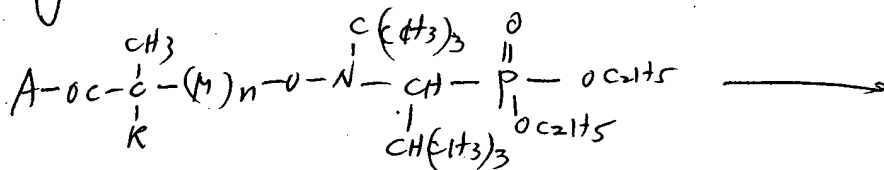
Earliest Priority Date: _____

Search Topic:

Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched. Include the elected species or structures, keywords, synonyms, acronyms, and registry numbers, and combine with the concept or utility of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc., if known.

For Sequence Searches Only Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.

I, such a group of inty cpl of form (I)
bg: (see claim 9-16)



* X is 1 or 2

* Z is CH₂=CHCH₂

CH₂=CH-CH₂-NH,
etc

* A is OK'
R' is alkyl

II such a group of inty cpl
of claim 13, 14, 15

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Searcher: _____

Searcher Phone #: _____

Searcher Location: _____

Date Searcher Picked Up: _____

Date Completed: _____

Searcher Prep & Review Time: _____

Online Time: _____

Type of Search

____ NA Sequence (#)

____ AA Sequence (#)

____ Structure (#)

____ Bibliographic

____ Litigation

____ Fulltext

____ Other

Vendors and cost where applicable

____ STN ____ Dialog

____ Questel/Orbit ____ Lexis/Nexis

____ Westlaw ____ WWW/Internet

____ In-house sequence systems

____ Commercial ____ Oligomer ____ Score/Length

____ Interference ____ SPDI ____ Encode/Transl

____ Other (specify)



STIC Search Results Feedback Form

EIC17000

Questions about the scope or the results of the search? Contact *the EIC searcher* or contact:

Kathleen Fuller, EIC 1700 Team Leader
571/272-2505 REMSEN 4B28

Voluntary Results Feedback Form

- I am an examiner in Workgroup: Example: 1713
- Relevant prior art **found**, search results used as follows:

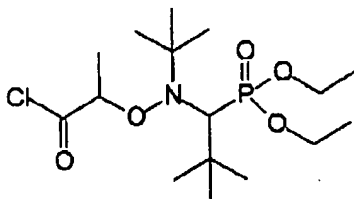
- ☐ 102 rejection
- ☐ 103 rejection
- ☐ Cited as being of interest.
- ☐ Helped examiner better understand the invention.
- ☐ Helped examiner better understand the state of the art in their technology.

Types of relevant prior art found

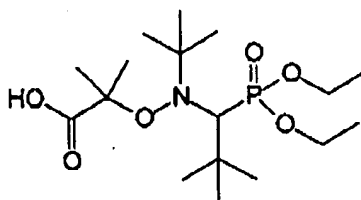
- ☐ Foreign Patent(s)
- ☐ Non-Patent Literature
(journal articles, conference proceedings, new product announcements etc.)

- Relevant prior art **not found**:

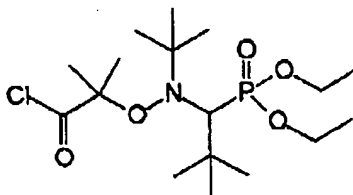
- ☐ Results verified the lack of relevant prior art (helped determine patentability)
- ☐ Results were not useful in determining patentability or understanding the invention



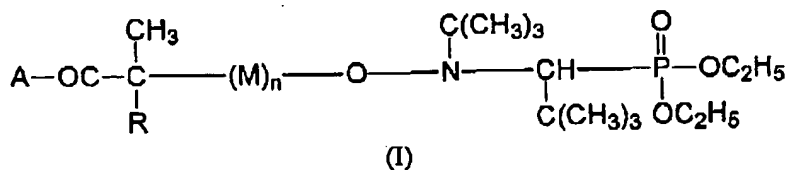
7. (withdrawn) The alkoxyamine of Claim 1 wherein said alkoxyamine is 2-Methyl-2-[N-tert-butyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]propionic acid :



8. (withdrawn) The alkoxyamine of Claim 1 wherein said alkoxyamine is 2-Methyl-2-[N-tert-butyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]propionyl chloride:

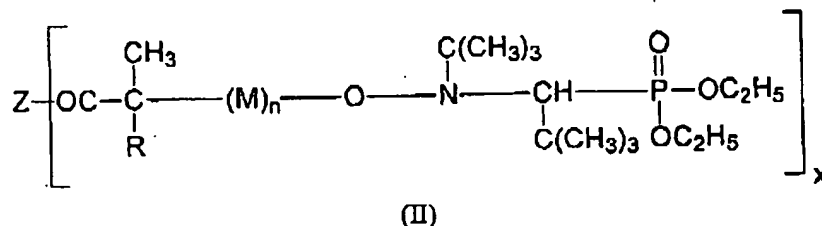


9. (previously presented) A method for preparing a polymerised or non-polymerized mono- or polyalkoxyamine comprising reacting an alkoxyamine of formula (I):



in which A represents a hydroxyl radical, a radical $\text{R}'\text{O}\cdot$ in which R' represents a linear or branched alkyl residue containing a number of carbon atoms ranging from 1 to 6; a radical $\text{MeO}\cdot$ in which Me represents an alkali metal; an $\text{H}_4\text{N}^+\cdot$, $\text{Bu}_4\text{N}^+\cdot$ or $\text{Bu}_3\text{HN}^+\cdot$ radical; a chlorine atom; R represents a hydrogen atom or a methyl radical; M is a free-radical-polymerizable vinyl monomer sequence; n is an integer that may be

equal to 0; to form a polymerised or nonpolymerized mono- or polyalkoxyamine of the formula (II):



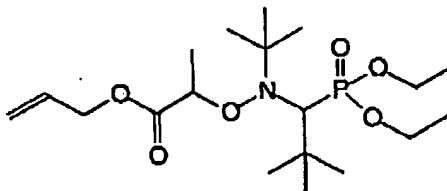
in which R and n have the same meaning as in formula (I); x is an integer at least equal to 1; Z represents a mono- or polyfunctional structure chosen from the structures given below in a non-limiting manner: $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-$, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}-$, $\text{CH}_3-(\text{OCH}_2\text{CH}_2)_p-\text{O}-$, $-\text{O}-(\text{CH}_2)_q-\text{O}-$, p and q being integers at least equal to one, or more generally derived from compounds such as alcohols, polyols, amines, polyamines, epoxides, polyepoxides, esters, polyesters, amides, polyamides, imines, polyimines, polycarbonates, polyurethanes and silicones.

10. (previously presented) The method of Claim 9 wherein said alkali metal ME is selected from the group consisting of Li, Na, K, and mixtures thereof.

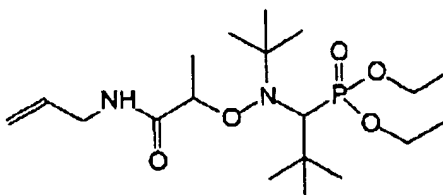
11. (previously presented) The method of claim 9 in which M is styrene, substituted styrenes, dienes, acrylic monomers, methacrylic monomers, acrylonitrile, acrylamide and its derivatives, vinylpyrrolidinone or a mixture of at least two abovementioned monomers.

12. (previously presented) The method of Claim 11 wherein the acrylic monomer is selected from the group consisting of acrylic acid or alkyl acrylates and mixtures thereof; and the methacrylic monomer is selected from the group consisting of methacrylic acid or alkyl methacrylates and mixtures thereof.

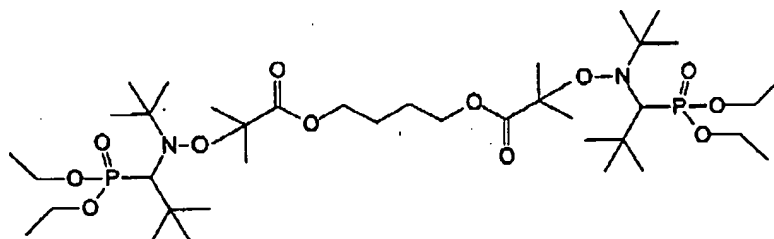
13. (previously presented) The method of Claim 9 wherein said method forms allyl 2-[N-tert-butyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]propionate:



14. (previously presented) The method of Claim 9 wherein said method forms N-allyl-2-[N-tert-butyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]propionamide:



15. (previously presented) The method of Claim 9 wherein said method forms a dialkoxyamine of formula:



16. (previously presented) The method of claim 9 wherein said method forms a compound of formula (II) in which $x=1$, $n=0$, $R=CH_3$ and $Z=CH_3(OCH_2CH_2)_pO-$.

g of the acid form of the alkoxyamine referred to as AA-SG1 in the form of a white powder (yield = 90%).

Characterization of 2-[N-tert-butyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl)-aminoxy]propionic acid :

m.p. = 145°C

^{31}P NMR (121.59 MHz, CDCl_3) : \square 27.65 (s, Dia I, 65%). 24.60 (s, Dia II, 35%).

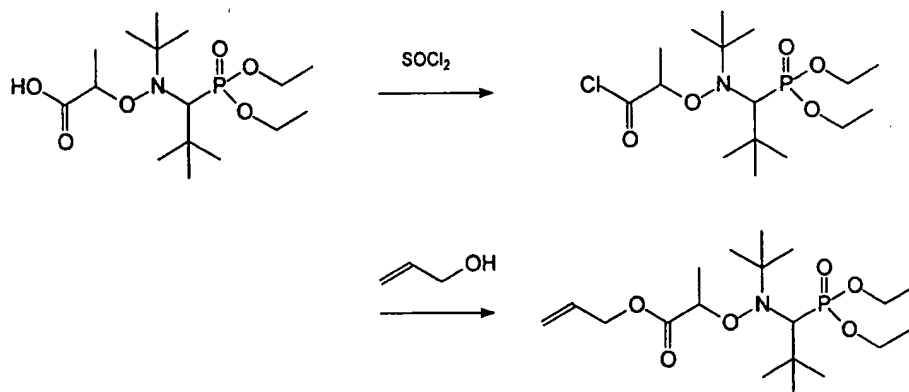
^1H NMR (300 MHz, CDCl_3) : Dia I. \square 4.68 (q, $J = 6$ Hz, 1H), 3.90-4.35 (m, 4H), 3.38 (d, $J = 27$ Hz, 1H), 1.61 (d, $J = 6$ Hz, 3H), 1.34 (m, 6H), 1.20 (s, 9H), 1.19 (s, 9H).

Dia II. \square 4.54 (q, $J = 9$ Hz, 1H), 3.90-4.35 (m, 4H), 3.38 (d, $J = 27$ Hz, 1H), 1.49 (d, $J = 9$ Hz, 3H), 1.31 (t, $J = 9$ Hz, 6H), 1.17 (s, 9H), 1.12 (s, 9H).

^{13}C NMR (75.54 MHz, CDCl_3) : Dia I. \square 174.17 (s, COOH), 81.46 (s, CH-O), 68.12 (d, $J = 139$ Hz, CH-P), 62.53 (s, $\text{N-C(CH}_3)_3$), 62.65 (d, $J = 5.28$ Hz, CH_2), 59.86 (d, $J = 7.55$ Hz, CH_2), 35.54 (d, $J = 4.53$ Hz, $\text{CH-C(CH}_3)_3$), 30.24 (d, $J = 6.8$ Hz, $\text{CH-C(CH}_3)_3$), 27.80 (s, $\text{N-C(CH}_3)_3$), 19.35 (s, CH-CH_3), 16.31 (d, $J = 5.29$ Hz, CH_2CH_3), 16.04 (d, $J = 6.8$ Hz, CH_2CH_3). Dia II. \square 174.78 (s, COOH), 81.31 (s, CH-O), 69.47 (d, $J = 141.26$ Hz, CH-P), 62.53 (s, $\text{N-C(CH}_3)_3$), 62.22 (d, $J = 6.8$ Hz, CH_2), 59.86 (d, $J = 7.55$ Hz, CH_2), 35.59 (d, $J = 2.26$ Hz, $\text{CH-C(CH}_3)_3$), 29.85 (d, $J = 6.04$ Hz, $\text{CH-C(CH}_3)_3$), 27.72 (s, $\text{N-C(CH}_3)_3$), 18.43 (s, CH-CH_3), 16.35 (d, $J = 6.8$ Hz, CH_2CH_3), 16.13 (d, $J = 6.8$ Hz, CH_2CH_3).

Example 2 :

Esterification of AA-SG1



2 g of AA-SG1 (5.4 mmol) dissolved in 25 ml of dichloromethane predried over molecular sieves are placed in a 100 ml round-bottomed flask under a nitrogen atmosphere.

1.9 g of thionyl chloride (16.2 mmol) are added and the mixture is left to react for 45 minutes at room temperature. The reaction mixture is evaporated under vacuum to give the acid chloride of the alkoxyamine in the form of an oil, which is used in the subsequent synthesis without further purification.

- 5 The acid chloride obtained above is redissolved in 30 ml of ethyl ether (predried by distillation over sodium-benzophenone). A mixture containing 0.62 g of allyl alcohol (10.8 mmol), 0.55 g of triethylamine (5.4 mmol), 0.13 g of 4-dimethylaminopyridine (1.1 mmol) and 10 ml of ether is added thereto at room temperature. The mixture is left to react for 2 hours at room temperature. The reaction mixture is filtered, washed with aqueous 0.1 M HCl solution and then washed with aqueous 5% potassium bicarbonate solution. The organic phase is evaporated to give 1.53 g of the allylic amide of the alkoxyamine AA-SG1 (yield = 60%).

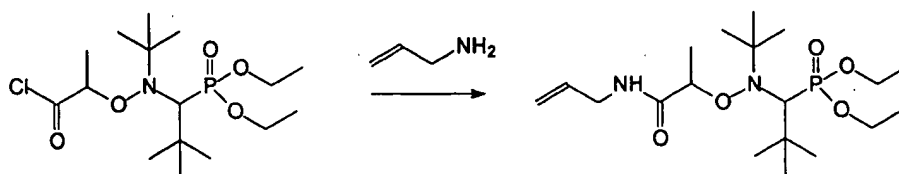
15 Characterization of allyl 2-[N-tert-butyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl)-aminoxy]propionate :

- ³¹P NMR (121.59 MHz, CDCl₃) : □ 23.23 (s, Dia I, 80%). 22.61 (s, Dia II, 20%).
- ¹H NMR (300 MHz, CDCl₃) : □ 5.96-5.87 (m, 2H, dia I+II), 5.37-5.23 (m, 4H, dia I+II), 4.64-4.58 (m, 6H, dia I+II), 4.25-3.93 (m, 8H, dia I+II), 3.37 (d, J = 27 Hz, 1H, dia II), 3.27 (d, J = 24 Hz, dia I), 1.53 (d, J = 9 Hz, 3H, dia I), 1.50 (d, J = 6 Hz, 3H, dia II), 1.36-1.27 (m, 12H, dia I+II), 1.17 (s, 9H, dia II), 1.16 (s, 9H, dia I), 1.14 (s, 9H, dia II), 1.11 (s, 9H, dia I).
- 25 ¹³C NMR (75.54 MHz, CDCl₃) : Dia I. □ 173.43 (s, CO), 131.69 (s, CH=CH₂), 118.50 (s, CH=CH₂), 82.49 (s, CH-ON), 69.51 (d, J = 139.75 Hz, CH-P), 64.90 (s, O-CH₂-CH), 61.71 (d, J = 6.04 Hz, CH₂), 61.52 (s, N-C(CH₃)₃), 58.67 (d, J = 7.55 Hz, CH₂), 35.45 (d, J = 5.28 Hz, CH-C(CH₃)₃), 29.46 (d, J = 5.28 Hz, CH-C(CH₃)₃), 27.81 (s, N-C(CH₃)₃), 19.19 (s, CH-CH₃), 16.40 (d, J = 5.29 Hz, CH₂CH₃), 16.10 (d, J = 6.8 Hz, CH₂CH₃). Dia II. □
- 30 172.03 (s, CO), 132.06 (s, CH=CH₂), 117.97 (s, CH=CH₂), 82.49 (s, CH-ON), 69.17 (d, J = 139.75 Hz, CH-P), 64.83 (s, O-CH₂-CH), 61.81 (d, J = 8.3 Hz, CH₂), 61.27 (s, N-C(CH₃)₃), 58.82 (d, J = 6.8 Hz, CH₂), 35.10 (d, J = 5.28 Hz, CH-C(CH₃)₃), 30.17 (d, J = 6.04 Hz, CH-C(CH₃)₃), 27.87 (s, N-C(CH₃)₃), 17.73 (s, CH-CH₃), 15.80 (d, J = 6.8 Hz, CH₂CH₃), 15.77 (d, J = 6.8 Hz, CH₂CH₃).

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Example 3 :

Amidation of AA-SG1



The acid chloride of the alkoxyamine AA-SG1 is synthesized in the same manner as in Example 2.

- 5 2.1 g of acid chloride (5.4 mmol) are dissolved in 30 ml of ethyl ether. A mixture containing 0.62 g of allylamine (10.8 mmol), 0.55g of triethylamine (5.4 mmol), 0.13 g of 4-dimethylaminopyridine (1.1 mmol) and 10 ml of ether is added at room temperature. The mixture is left to react for two hours at room temperature. The reaction mixture is filtered, washed with aqueous 0.1 M HCl solution and then washed with aqueous 5% potassium bicarbonate solution. The organic phase is evaporated to give 1.53 g of the allylic amide of the alkoxyamine AA-SG1 (yield =70%)

Characterization of N-allyl-2-[N-tert-butyl-N-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]propionamide :

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^{31}P NMR (121.59 MHz, CDCl_3) : \square 27.42 (s, Dia I, 35%). 27.05 (s, Dia II, 65%).

^1H NMR (300 MHz, CDCl_3) : Dia I \square 8.61 (b, NH, 1H), 5.96-5.83 (m, 1H), 5.19 (dq, $J_{\text{HH}} = 1.5$ Hz, $J_{\text{HH}} = 18\text{Hz}$, 1H), 5.08 (dq, $J_{\text{HH}} = 1.5$ Hz, $J_{\text{HH}} = 9\text{Hz}$, 1H), 4.48 (q, $J = 6\text{Hz}$, 1H), 4.29-3.97 (m, 5H), 3.67 (m, 1H), 3.35 (d, $J = 27$ Hz), 1.51 (d, $J = 6$ Hz, 3H), 1.35-1.28 (m, 6H), 1.21 (s, 9H), 1.08 (s, 9H). Dia II. 7.74 (b, NH, 1H), 5.96-5.83 (m, 1H), 5.21(d, $J = 18$ Hz, 1H), 205.11(d, $J = 9$ Hz, 1H), 4.51 (q, $J = 9\text{Hz}$, 1H), 4.20-3.95 (m, 5H), 3.88 (t, $J = 7.5\text{Hz}$, 1H), 3.28 (d, $J = 24$ Hz), 1.63 (d, $J = 6$ Hz, 3H), 1.36-1.28 (m, 6H), 1.25 (s, 9H), 1.24 (s, 9H).

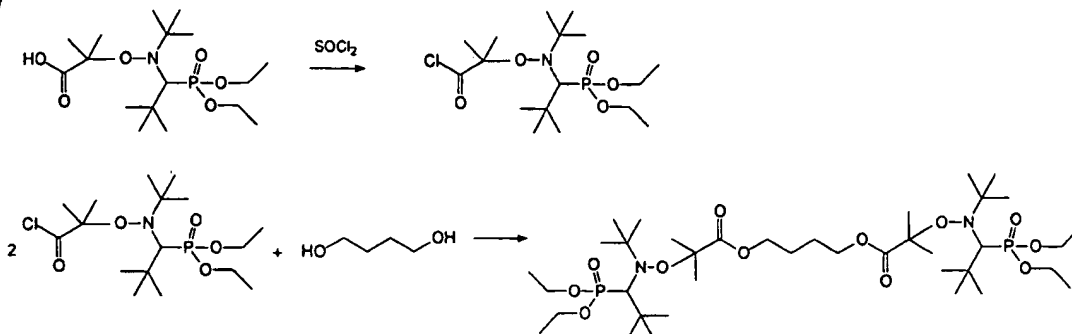
25

^{13}C NMR (75.54 MHz, CDCl_3) : Dia I. \square 173.55 (s, CO), 134.40 (s, $\text{CH}=\text{CH}_2$), 115.18 (s, $\text{CH}=\text{CH}_2$), 81.76 (s, CH-ON), 68.56 (d, $J = 137.48$ Hz, CH-P), 62.17 (s, $\text{N-C}(\text{CH}_3)_3$), 61.56 (d, $J = 6.04$ Hz, CH_2), 59.64 (d, $J = 7.55$ Hz, CH_2), 41.06 (s, N-CH_2), 35.36 (d, $J = 5.28$ Hz, $\text{CH-C}(\text{CH}_3)_3$), 29.69 (d, $J = 6.04$ Hz, $\text{CH-C}(\text{CH}_3)_3$), 28.15 (s, $\text{N-C}(\text{CH}_3)_3$), 19.21 (s, CH-CH_3), 16.25 (d, $J = 6.04$ Hz, CH_2CH_3), 15.91 (d, $J = 6.8$ Hz, CH_2CH_3). Dia II. \square 173.42 (s, CO), 134.27 (s, $\text{CH}=\text{CH}_2$), 116.30 (s, $\text{CH}=\text{CH}_2$), 83.05 (s, CH-ON), 69.25 (d, $J = 137.48$ Hz, CH-P), 62.85 (s, $\text{N-C}(\text{CH}_3)_3$), 61.55 (d, $J = 6.04$ Hz, CH_2), 60.04 (d, $J = 7.55$ Hz, CH_2), 41.46 (s, N-CH_2), 35.33 (d, $J = 5.28$ Hz, $\text{CH-C}(\text{CH}_3)_3$), 30.06 (d, $J = 5.28$ Hz, $\text{CH-C}(\text{CH}_3)_3$), 28.38 (s, $\text{N-C}(\text{CH}_3)_3$), 19.55 (s, CH-CH_3), 16.55 (d, $J = 6.80$ Hz, CH_2CH_3), 16.30 (d, $J = 6.8$ Hz, CH_2CH_3).

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Example 5 :

Synthesis of a dialkoxyamine from the alkoxyamine methylpropionic acid-SG1.



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The alkoxyamine methylpropionic acid-SG1 is prepared according to Example 4.

10 g of alkoxyamine methylpropionic acid-SG1 (26 mmol) and 50 ml of dichloromethane (dried over calcium hydride) are introduced into a 250 ml reactor purged with nitrogen. 6.2 g of SOCl_2 (52 mmol) are added, via a dropping funnel, at room temperature. The mixture is left to react for 2 hours at room temperature with stirring and under a gentle stream of nitrogen. Evaporation under vacuum is performed to remove the excess SOCl_2 and the solvent. The acid chloride of the alkoxyamine is obtained, and is used in the subsequent synthesis without further purification.

The resulting oil is redissolved in 50 ml of dry dichloromethane. A mixture containing 1.2 g of 1,4-butanediol (13 mmol), 2.6 g of triethylamine (26 mmol) and 0.3 g of 4-dimethylaminopyridine (2.6 mmol) dissolved in 10 ml of dichloromethane is placed in the dropping funnel, under a nitrogen atmosphere. The above mixture is added dropwise to the reactor and the mixture is then left to react for three hours at room temperature. The reaction mixture is filtered, washed with a KHCO_3 solution and then washed with water. The organic phase is recovered, dried over magnesium sulphate and evaporated to dryness under vacuum at room temperature. A solid is obtained, which is washed with cold pentane to give 5.2 g of dialkoxyamine (yield = 50%).

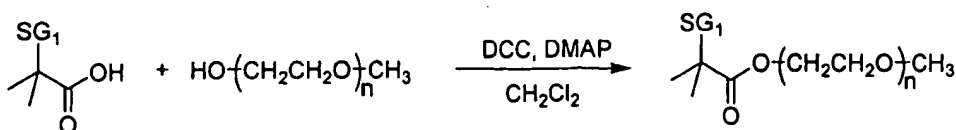
The dialkoxyamine was characterized by proton, carbon-13 and phosphorus NMR.

^{31}P NMR (CDCl_3) : $\delta = 26$ ppm

25

Example 6:

Coupling between the alkoxyamine methylpropionic acid-SG1 and a POE-Ome block ($\text{Mn} = 750 \text{ g.mol}^{-1}$) :



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Bib Data Sheet

CONFIRMATION NO. 5047

SERIAL NUMBER 10/813,822	FILING DATE 03/31/2004 RULE	CLASS 514	GROUP ART UNIT 1626	ATTORNEY DOCKET NO. FR-AM 1946 NP	
APPLICANTS Jean-luc Couturier, Lyon, FRANCE; Oliver Guerret, Mazerolles, FRANCE; Denis Bertin, Plan De Cuques, FRANCE; Didier Gignes, Marseille, FRANCE; Sylvain Marque, Antraigues Sur Volane, FRANCE; Paul Tordo, Marseille, FRANCE; Pierre-Emmanuel Dufils, Carry Le Rouet, FRANCE;					
** CONTINUING DATA *****					
** FOREIGN APPLICATIONS ***** FRANCE 03.03999 04/01/2003					
IF REQUIRED, FOREIGN FILING LICENSE GRANTED ** 06/10/2004					
Foreign Priority claimed <input checked="" type="checkbox"/> yes <input type="checkbox"/> no 35 USC 119 (a-d) conditions <input type="checkbox"/> met <input checked="" type="checkbox"/> no <input type="checkbox"/> Met after Verified and Acknowledged	Examiner's Signature 	STATE OR COUNTRY FRANCE	SHEETS DRAWING 0	TOTAL CLAIMS 16	INDEPENDENT CLAIMS 2
ADDRESS 31684 ARKEMA INC. PATENT DEPARTMENT - 26TH FLOOR 2000 MARKET STREET PHILADELPHIA , PA 19103-3222					
TITLE Alkoxyamines derived from beta-phosphorylated nitroxides, and use thereof for preparing polymerized or non-polymerized mono-or polyalkoxyamines					
			<input type="checkbox"/> All Fees		

=> fil reg

FILE 'REGISTRY' ENTERED AT 09:25:33 ON 24 JUL 2006

=> d his

FILE 'HCAPLUS' ENTERED AT 07:49:13 ON 24 JUL 2006

L1 1 S US20050065119/PN
SEL RN

FILE 'REGISTRY' ENTERED AT 07:49:37 ON 24 JUL 2006

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L5 116 S L3 FUL
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L6 10 S L5 AND L2
L7 58 S L5 NOT 1-100/NR
L8 58 S L5 NOT L7
L9 STR L3
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L13 1 S 763105-79-9/RN
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L17 14 S L9 FUL SUB=L5

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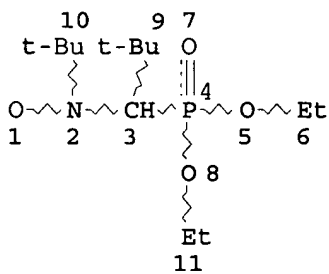
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L23 3 S L18 OR L22
L24 1 S L11
L25 17 S L19 OR L24
L26 19 S L23 OR L25

FILE 'CASREACT' ENTERED AT 09:17:51 ON 24 JUL 2006

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L29 8 S L27 FUL
SAV L29 SHI822A/A

=> d que 126

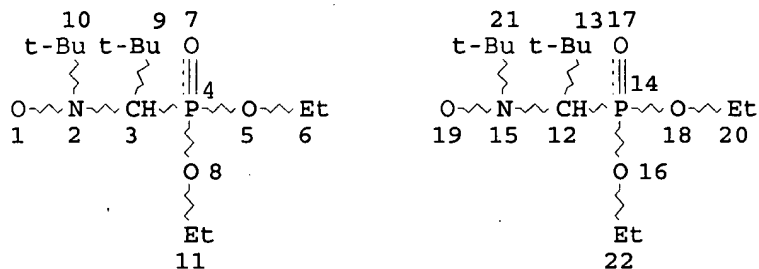
L3 STR



NODE ATTRIBUTES:
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 DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
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 NUMBER OF NODES IS 11

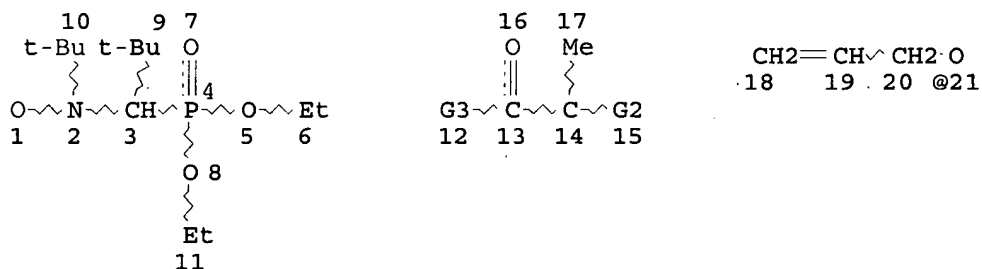
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 L9 STR



NODE ATTRIBUTES:
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 DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
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 NUMBER OF NODES IS 22

STEREO ATTRIBUTES: NONE
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 L12 1 SEA FILE=REGISTRY ABB=ON 763105-81-3/RN
 L13 1 SEA FILE=REGISTRY ABB=ON 763105-79-9/RN
 L14 STR



CH2=CH^CH2-NH 22 23 24 @25 O~G4~O 26 27 @28 CH2^G5~O 29 30 @31 O~Ak @32 @33

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 VAR G3=21/25/28/31
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 REP G5=(1-5) 32-29 33-31
 NODE ATTRIBUTES:
 DEFAULT MLEVEL IS ATOM
 DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS 33

STEREO ATTRIBUTES: NONE

L16 4 SEA FILE=REGISTRY SUB=L5 SSS FUL L14
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L19 17 SEA FILE=HCAPLUS ABB=ON L17
L20 2 SEA FILE=HCAPLUS ABB=ON L12
L21 3 SEA FILE=HCAPLUS ABB=ON L13
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L23 3 SEA FILE=HCAPLUS ABB=ON L18 OR L22
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L25 17 SEA FILE=HCAPLUS ABB=ON L19 OR L24
L26 19 SEA FILE=HCAPLUS ABB=ON L23 OR L25

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FILE 'HCAPLUS' ENTERED AT 09:25:49 ON 24 JUL 2006

=> d l26 1-19 ibib abs hitstr hitind

✓ L26 ANSWER 1 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2006:558238 HCAPLUS
DOCUMENT NUMBER: 145:28691
TITLE: Cast plates with improved impact resistance
based on methyl methacrylate copolymers
INVENTOR(S): Guerret, Olivier; Chenard, Jean-Yves; Ederle,
Yannick
PATENT ASSIGNEE(S): Arkema, Fr.
SOURCE: PCT Int. Appl., 57 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: French
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2006061523	A1	20060615	WO 2005-FR3087	2005 1209
<p>W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW</p> <p>RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM</p>				
FR 2879205	A1	20060616	FR 2004-13186	2004

PRIORITY APPLN. INFO.:

FR 2004-13186

1210
A
2004
1210

US 2005-647056P

P
2005
0126

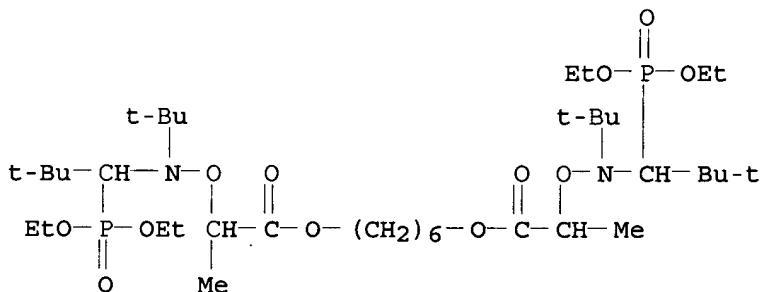
AB Me methacrylate (I) copolymers that provide cast-molded sheets with improve impact strength are manufactured by (1) polymerization of a monomer in the presence of ≥ 1 alkoxyamine having ≥ 2 groups formed from nitroxides [e.g., $[\text{Me}_3\text{CCH}[\text{P}(\text{:O})(\text{OEt})_2]\text{N}(\text{CMe}_3)\text{OC HMeCO}_2(\text{CH}_3)]_2$] at temps. sufficient to activate the alkoxyamine to form a core chain (glass-transition temperature $< 0^\circ$), (2) reaction of the core chain optionally, containing unreacted core-chain monomers with monomers destined to form branches (glass-transition temperature $> 0^\circ$), and (3) polymerization of I and, optionally, other monomers in the presence of the product of (2) and ≥ 1 radical initiator.

IT 300811-94-3

(cast plates with improved impact resistance based on Me methacrylate copolymers manufactured in presence of multifunctional alkoxyamines)

RN 300811-94-3 HCAPLUS

CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, 1,6-hexanediyl ester, 6,6'-dioxide (9CI) (CA INDEX NAME)



CC 37-3 (Plastics Manufacture and Processing)

IT 300811-94-3

(cast plates with improved impact resistance based on Me methacrylate copolymers manufactured in presence of multifunctional alkoxyamines)

REFERENCE COUNT:

2

THERE ARE 2 CITED REFERENCES AVAILABLE
FOR THIS RECORD. ALL CITATIONS AVAILABLE
IN THE RE FORMAT

L26 ANSWER 2 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2006:506 HCAPLUS

DOCUMENT NUMBER: 144:254481

TITLE: Nitroxide-mediated radical polymerization of
2-(dimethylamino)ethyl acrylate and its
sequential block copolymerization with styrene
and n-butyl acrylate

AUTHOR(S): Bian, Kejian; Cunningham, Michael F.

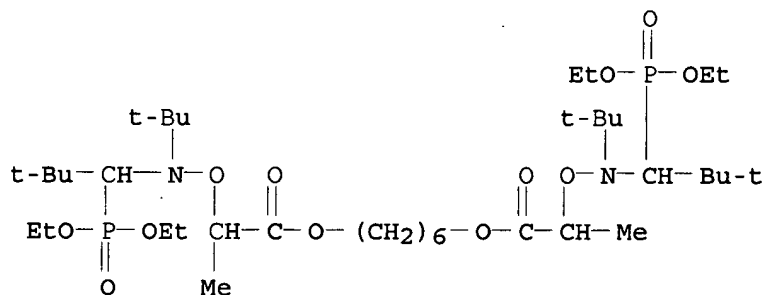
CORPORATE SOURCE: Department of Chemical Engineering, Queen's University, Kingston, ON, K7L 3N6, Can.
 SOURCE: Journal of Polymer Science, Part A: Polymer Chemistry (2005), Volume Date 2006, 44(1), 414-426
 CODEN: JPACEC; ISSN: 0887-624X
 PUBLISHER: John Wiley & Sons, Inc.
 DOCUMENT TYPE: Journal
 LANGUAGE: English

AB Nitroxide-mediated radical polymerization (NMRP) of 2-(dimethylamino)ethyl acrylate (DMAEA) was carried out at 100-120 °C, initiated by MONAMS, an alkoxyamine based on N-tert-butyl-N-(1-diethyl phosphono-2,2-dimethylpropyl)nitroxide, SG1. Controlled polymerization can be achieved by the addition of free SG1 (the initial molar ratio of SG1 to MONAMS ranged from 0.06 to 0.12), giving a linear first-order kinetic plot up to 55-70% conversion depending on the reaction conditions. The mol. wts. show a near linear increase with conversion; however, they deviate to some extent with theor. values. SG1-mediated polymerization of DMAEA at 112 °C is also controlled in organic solvents (N,N-dimethylformide, anisole, xylene). Polymerization rate increases with increasing solvent polarity. Chain transfer to polymer produces .apprx.1 mol % branches in bulk and 1.2-1.9 mol % in organic solvents, typical of those for acrylates. From poly(styrene) (pS) and poly(Bu acrylate) (pBA) macroinitiators, amphiphilic di- and triblock copolymers p(S-b-DMAEA), p(DMAEA-b-S-b-DMAEA), p(BA-b-DMAEA), and p(DMAEA-b-BA-b-DMAEA) were synthesized via NMRP at 110 °C. Polymers were characterized by GPC, NMR, surface tension measurements, and DSC.

IT 300811-94-3
 (nitroxide-mediated radical polymerization of (dimethylamino)ethyl acrylate and its sequential block copolymn. with styrene and Bu acrylate)

RN 300811-94-3 HCAPLUS

CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, 1,6-hexanediyl ester, 6,6'-dioxide (9CI) (CA INDEX NAME)



CC 35-4 (Chemistry of Synthetic High Polymers)

IT 188526-94-5 300811-93-2 300811-94-3
 (nitroxide-mediated radical polymerization of (dimethylamino)ethyl acrylate and its sequential block copolymn. with styrene and Bu acrylate)

REFERENCE COUNT: 40 THERE ARE 40 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L26 ANSWER 3 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2005:1162780 HCAPLUS

DOCUMENT NUMBER: 144:70138

TITLE: Nitroxide-Mediated Controlled Free-Radical Emulsion Polymerization Using a Difunctional Water-Soluble Alkoxyamine Initiator. Toward the Control of Particle Size, Particle Size Distribution, and the Synthesis of Triblock Copolymers

AUTHOR(S): Nicolas, Julien; Charleux, Bernadette; Guerret, Olivier; Magnet, Stephanie

CORPORATE SOURCE: Laboratoire de Chimie Macromoléculaire, Université Pierre et Marie Curie, Paris, 75252, Fr.

SOURCE: Macromolecules (2005), 38(24), 9963-9973
CODEN: MAMOBX; ISSN: 0024-9297

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

AB A novel dialkoxyamine bearing two carboxylic acid groups was synthesized by the addition of a high dissociation rate constant alkoxyamine onto tri(ethylene glycol) diacrylate. This dialkoxyamine was first successfully used as an initiator for the bulk polymns. of Bu acrylate and styrene. Then the sodium salt counterpart was used as a water-soluble initiator in the emulsion polymns. of Bu acrylate and styrene via a multistep process. Owing to its unique structure with two carboxylate salts remaining covalently bound to the chain and hence locked at the particle surface, very stable latexes were recovered with, for the first time, small particles and narrow particle size distributions. The emulsion process was successfully applied to the synthesis of well-defined poly(Bu acrylate) and polystyrene homopolymers as well as polystyrene-b-poly(Bu acrylate)-b-polystyrene triblock copolymer. This work represents the first successful attempt of the synthesis of a complex architecture together with the control of average diameter and particle size distribution in nitroxide-mediated polymerization in emulsion, which is of high industrial and academic interest.

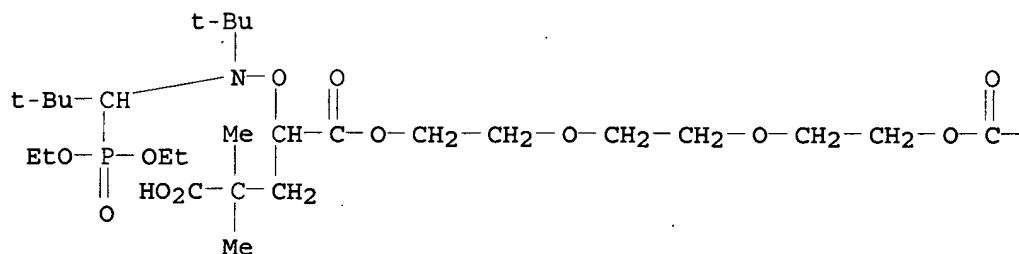
IT 871982-25-1P 871982-26-2P

(preparation of a difunctional water-soluble alkoxyamine initiator for nitroxide-mediated controlled free-radical emulsion polymerization)

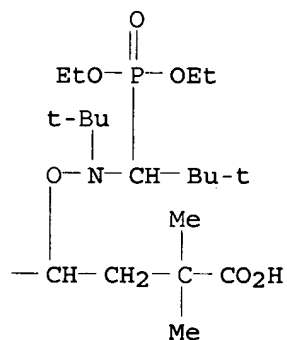
RN 871982-25-1 HCAPLUS

CN 6,9,12,15-Tetraoxaeicosanedioic acid, 4,17-bis[[[1-(diethoxyphosphinyl)-2,2-dimethylpropyl](1,1-dimethylethyl)amino]oxy]-2,2,19,19-tetramethyl-5,16-dioxo- (9CI)
(CA INDEX NAME)

PAGE 1-A



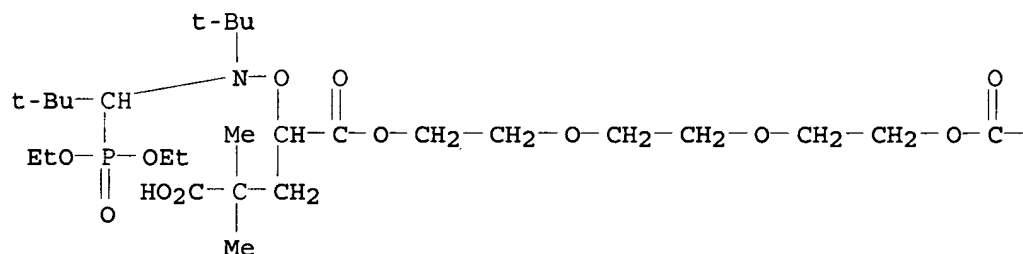
PAGE 1-B



RN 871982-26-2 HCAPLUS

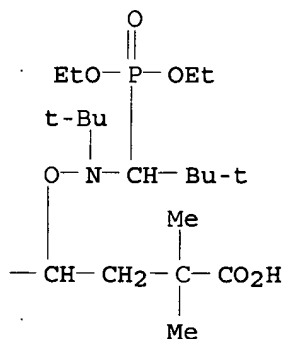
CN 6,9,12,15-Tetraoxaeicosanedioic acid, 4,17-bis[[[1-(diethoxyphosphinyl)-2,2-dimethylpropyl](1,1-dimethylethyl)amino]oxy]-2,2,19,19-tetramethyl-5,16-dioxo-, disodium salt (9CI) (CA INDEX NAME)

PAGE 1-A



● 2 Na

PAGE 1-B



CC 35-3 (Chemistry of Synthetic High Polymers)

IT 871982-25-1P 871982-26-2P

(preparation of a difunctional water-soluble alkoxyamine initiator for nitroxide-mediated controlled free-radical emulsion polymerization)

REFERENCE COUNT: 56 THERE ARE 56 CITED REFERENCES AVAILABLE
FOR THIS RECORD. ALL CITATIONS AVAILABLE
IN THE RE FORMAT

L26 ANSWER 4 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2005:727462 HCAPLUS

DOCUMENT NUMBER: 144:331825

TITLE: Use of a novel class of SG1-based
water-soluble dialkoxyamine in
nitroxide-mediated controlled-free radical
emulsion polymerization

AUTHOR(S): Nicolas, Julien; Charleux, Bernadette;
Guerret, Olivier; Magnet, Stephanie

CORPORATE SOURCE: Laboratoire de Chimie des Polymeres, CNRS -

UMR 7610 Universite Pierre et Marie Curie,
Paris, 75252/05, Fr.

SOURCE: Polymer Preprints (American Chemical Society,
Division of Polymer Chemistry) (2005), 46(2),
484-485

CODEN: ACPPAY; ISSN: 0032-3934

PUBLISHER: American Chemical Society, Division of Polymer
Chemistry

DOCUMENT TYPE: Journal; (computer optical disk)

LANGUAGE: English

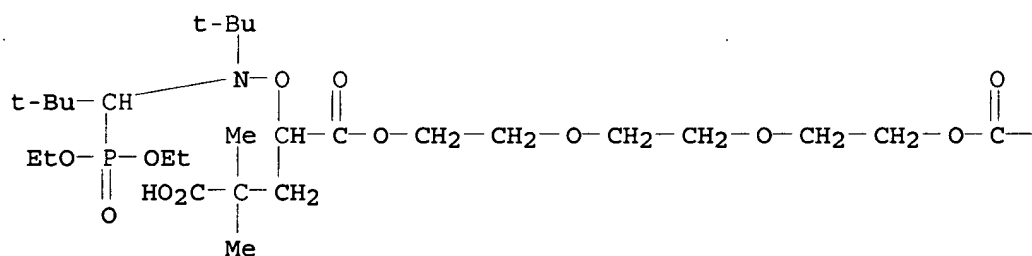
AB A novel SG1-based water-soluble dialkoxyamine was synthesized by
intermol. radical 1,2-addition of the MAMA alkoxyamine onto
tri(ethylene glycol) diacrylate. It was then used as an initiator
in nitroxide-mediated emulsion polymerization of n-Bu acrylate and
styrene through a multi-step process. Stable latexes were
recovered and all the features of a controlled system were
obtained whatever the monomer. Thanks to its unique structure,
the synthesis of a well-defined polystyrene-b-poly(n-Bu
acrylate)-b-polystyrene triblock copolymer by sequential monomer
addns. was also successfully performed.

IT 871982-25-1P
(nitroxide initiator; use of a novel class of SG1-based
water-soluble dialkoxyamine in nitroxide-mediated controlled-free
radical emulsion polymerization)

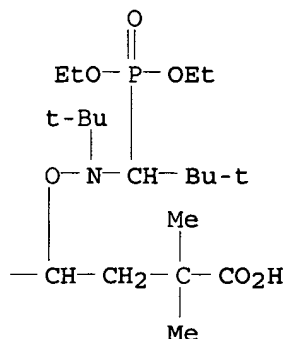
RN 871982-25-1 HCAPLUS

CN 6,9,12,15-Tetraoxaieicosanedioic acid, 4,17-bis[[[1-
(diethoxyphosphiny)-2,2-dimethylpropyl] (1,1-
dimethylethyl) amino]oxy]-2,2,19,19-tetramethyl-5,16-dioxo- (9CI)
(CA INDEX NAME)

PAGE 1-A



PAGE 1-B



CC 35-4 (Chemistry of Synthetic High Polymers)

IT 871982-25-1P

(nitroxide initiator; use of a novel class of SG1-based water-soluble dialkoxyamine in nitroxide-mediated controlled-free radical emulsion polymerization)

REFERENCE COUNT: 11 THERE ARE 11 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L76 ANSWER 5 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2005:727381 HCAPLUS

DOCUMENT NUMBER: 144:312375

TITLE: One step synthesis of NMP star polymer initiator for "core first" method

AUTHOR(S): Dufils, Pierre-Emmanuel; Gimes, Didier; Guerret, Olivier; Bertin, Denis; Tordo, Paul

CORPORATE SOURCE: UMR-CNRS 6517 Chimie Biologie et Radicaux Libres. CNRS-Universites d'Aix-Marseille, Marseille, 13397/20, Fr.

SOURCE: Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) (2005), 46(2), 328-329

CODEN: ACPPAY; ISSN: 0032-3934

PUBLISHER: American Chemical Society, Division of Polymer Chemistry

DOCUMENT TYPE: Journal; (computer optical disk)

LANGUAGE: English

AB Star polymer synthesis can be classified in two main strategies. Firstly, the "arm first" method involves coupling reaction between a multifunctional coupling agent and preformed length controlled, end functionalized polymer chains. Secondly, the "core first" method involves the synthesis of multiple polymer chains polymerized with a multifunctional initiator prepared through multi-step syntheses. In this paper we present a "core first" strategy which overcomes the drawbacks mentioned above and provide, in one step, a NMP star polymer precursor based on nitroxide SG1 from a new alkoxyamine and com. available compds. The initiator was synthesized by the intermol. radical addition of the alkoxyamine onto a triacrylate precursor to produce a trifunctional initiator carrying three nitroxide moieties. Star polymers were obtained by nitroxide mediated polymerization of styrene with the trifunctional initiator to provide a three arm star polymer. Although the synthesis of the initiator is not optimized, the preliminary

results indicate that the polymerization of styrene is controlled.

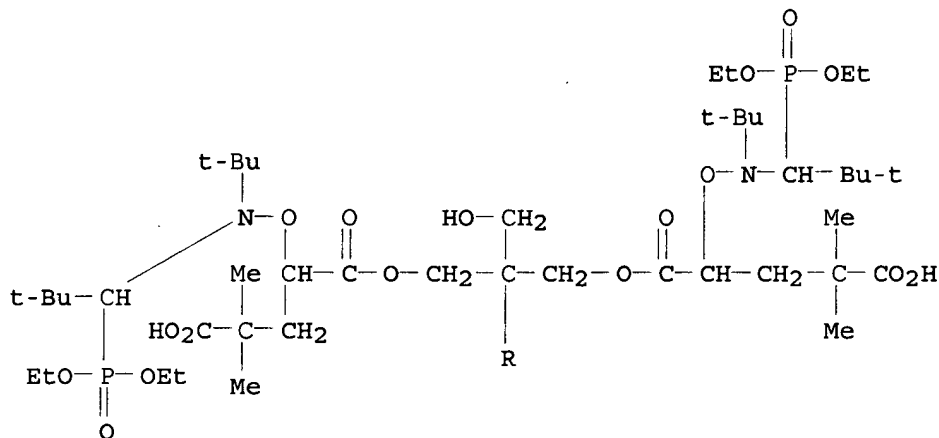
IT 880098-22-6P

(one step synthesis of NMP star polymer initiator)

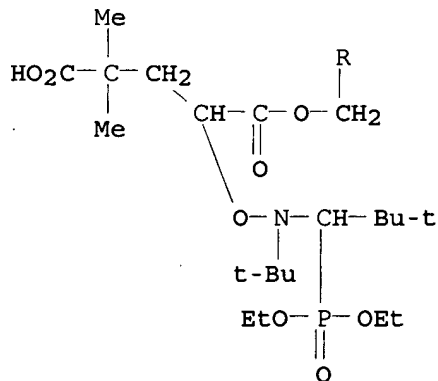
RN 880098-22-6 HCAPLUS

CN Pentanedioic acid, 4-[[[1-(diethoxyphosphinyl)-2,2-dimethylpropyl](1,1-dimethylethylamino)oxy]-2,2-dimethyl-, 5,5'-[2-[4-(2-carboxy-2-methylpropyl)-6,7-bis(1,1-dimethylethyl)-8-ethoxy-8-oxido-3-oxo-2,5,9-trioxa-6-aza-8-phosphaundec-1-yl]-2-(hydroxyethyl)-1,3-propanediyl] ester (9CI) (CA INDEX NAME)

PAGE 1-A



PAGE 2-A



CC 35-3 (Chemistry of Synthetic High Polymers)

IT 880098-22-6P

(one step synthesis of NMP star polymer initiator)

REFERENCE COUNT: 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

126 ANSWER 6 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2005:708387 HCAPLUS

DOCUMENT NUMBER: 143:347038

TITLE: SG1 based alkoxyamines as radical initiators for the synthesis of lactones and lactams

AUTHOR(S): Bertin, Denis; Gigmes, Didier; Marque, Sylvain R. A.; Tordo, Paul

CORPORATE SOURCE: UMR 6517, Universites d'Aix-Marseille I, II et III-CNRS, Marseille, 13397, Fr.

SOURCE: Tetrahedron (2005), 61(36), 8752-8761
CODEN: TETRAB; ISSN: 0040-4020

PUBLISHER: Elsevier B.V.

DOCUMENT TYPE: Journal

LANGUAGE: English

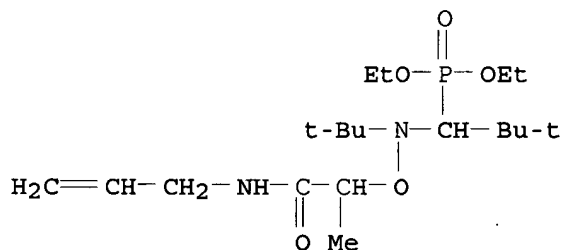
OTHER SOURCE(S): CASREACT 143:347038

AB Recently, it has been shown that alkoxy amine derivs. can be used as radical initiators in tin-free radical chemical. Thus, a method for the preparation of highly valuable alkoxyamines was developed, which involved ionic chemical and wherein a radical cyclization was triggered by thermal initiation. Following that procedure, bicyclic, spiro and eight-membered lactones were easily prepared in good yields with very high stereoselectivity. The reaction mechanism was discussed.

IT 763105-81-3P
(preparation of [[(tert-butyl)[methyl(oxo)propenylamino]ethoxy]amino]dimethylpropyl]phosphonic acid ester (SG1-initiator-based alkoxyamine derivative) and study of its thermal radical cyclization)

RN 763105-81-3 HCAPLUS

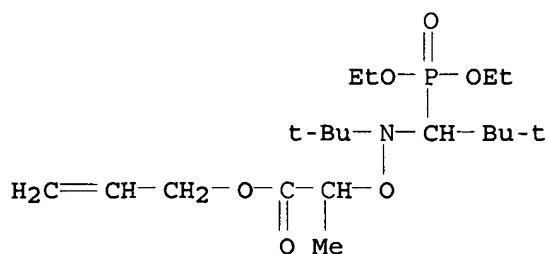
CN Phosphonic acid, [1-[(1,1-dimethylethyl)[1-methyl-2-oxo-2-(2-propenylamino)ethoxy]amino]-2,2-dimethylpropyl]-, diethyl ester (9CI) (CA INDEX NAME)



IT 763105-79-9P
(preparation of di(tert-butyl)(ethoxy)-3,7-dioxa-4-aza-6-phosphanonanoic acid propenyl ester oxide (SG1-initiator-based alkoxyamine derivative) and study of its thermal radical cyclization)

RN 763105-79-9 HCAPLUS

CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, 2-propenyl ester, 6-oxide (9CI) (CA INDEX NAME)



CC 27-20 (Heterocyclic Compounds (One Hetero Atom))

Section cross-reference(s): 22

IT 763105-81-3P

(preparation of [[(tert-butyl)[methyl(oxo)propenylamino]ethoxy]amino]dimethylpropyl]phosphonic acid ester (SG1-initiator-based alkoxyamine derivative) and study of its thermal radical cyclization)

IT 763105-79-9P

(preparation of di(tert-butyl)(ethoxy)-3,7-dioxa-4-aza-6-phosphanonanoic acid propenyl ester oxide (SG1-initiator-based alkoxyamine derivative) and study of its thermal radical cyclization)

REFERENCE COUNT: 48 THERE ARE 48 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

✓ L26 ANSWER 7 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2005:547687 HCAPLUS

DOCUMENT NUMBER: 143:80747

TITLE: Controlled radical acrylic copolymer thickeners

INVENTOR(S): Schmidt, Scott Charles; Callais, Peter Anthony; Macy, Noah Eliot; Guerrett, Olivier

PATENT ASSIGNEE(S): Arkema Inc., USA

SOURCE: PCT Int. Appl., 40 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005056739	A1	20050623	WO 2004-US34236	2004 1015

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW

RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI,

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 PRIORITY APPLN. INFO.: US 2003-525549P

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20031126

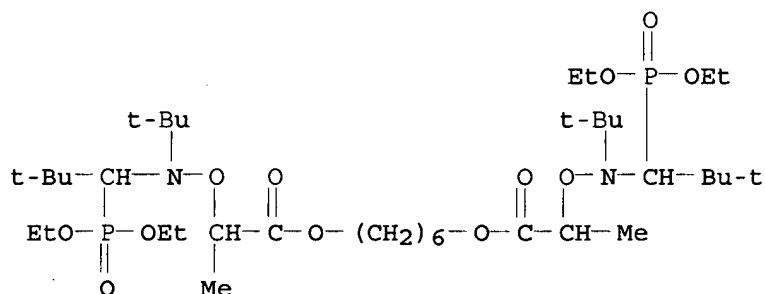
AB The present invention relates to acrylic block copolymers synthesized by a controlled radical process, and their use as thickeners in oil-based compns. The acrylic copolymers are especially useful as viscosity index improvers in lubricating oil.

IT 300811-94-3

(controlled living radical polymerized acrylic copolymer thickeners)

RN 300811-94-3 HCAPLUS

CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, 1,6-hexanediyl ester, 6,6'-dioxide (9CI) (CA INDEX NAME)



IC ICM C10M145-14

CC 51-8 (Fossil Fuels, Derivatives, and Related Products)
 Section cross-reference(s): 35, 36, 66

IT 188526-94-5 300811-93-2 300811-94-3

(controlled living radical polymerized acrylic copolymer thickeners)

REFERENCE COUNT: 7 THERE ARE 7 CITED REFERENCES AVAILABLE
 FOR THIS RECORD. ALL CITATIONS AVAILABLE
 IN THE RE FORMAT

L26 ANSWER 8 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2005:361852 HCAPLUS

DOCUMENT NUMBER: 142:411841

TITLE: Process for the preparation of
 polyalkoxyamines for use as initiators in
 radical polymerization

INVENTOR(S): Magnet, Stephanie; Guerret, Olivier;
 Couturier, Jean-Luc

PATENT ASSIGNEE(S): Arkema, Fr.

SOURCE: Eur. Pat. Appl., 14 pp.

CODEN: EPXXDW

DOCUMENT TYPE: Patent

LANGUAGE: French

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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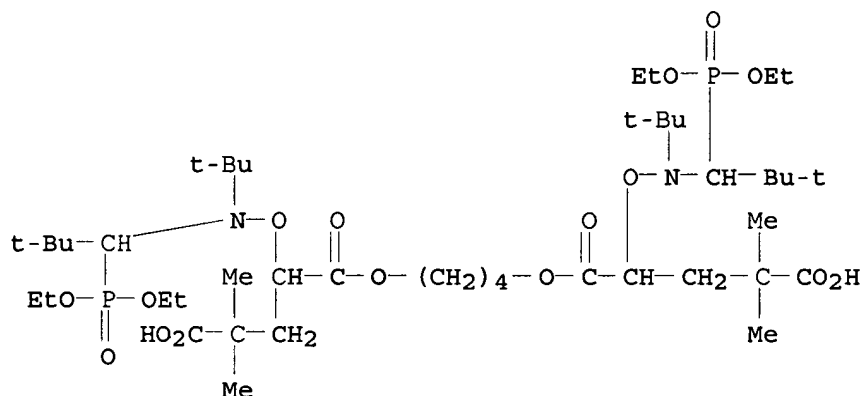
EP 1526138	A1	20050427	EP 2004-292480	2004 1019
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CA 2482501	AA	20050424	CA 2004-2482501	2004 1019
US 2005107577	A1	20050519	US 2004-969711	2004 1020
CN 1629136	A	20050622	CN 2004-10095971	2004 1022
JP 2005126442	A2	20050519	JP 2004-309512	2004 1025
PRIORITY APPLN. INFO.:			FR 2003-12452	A 2003 1024
			US 2003-514287P	P 2003 1024

AB Polyalkoxyamines, useful as initiators without purification from preparation mixts. for radical polymerization especially in manufacture of block polymers, are prepared by reaction of $R_1C(CO_2R_2)ON(CMe_3)CH(CMe_3)P(O)(OEt)_2$ ($R_1 = C_1-3$ alkyl, $R_2 = H$, C_1-8 alkyl, Ph, Li, Na, K, NH_4^+ , NBu_4^+ , or $NHBu_3^+$) (I) with $Z(CH:CH_2)_n$ [$Z = aryl$ or $Z_1(XCO)_n$; $Z_1 =$ polyfunctional compound such as polyol, $X = O, N$ having a C-containing group, or H, or S; $n \geq 2$] (II) optionally in a solvent at $0-90^\circ$ and I-II mol ratio $n-1.5n$. A typical polyalkoxyamine was manufactured by reaction of 42.1 g 2-bromo-2-methylpropionic acid 90 min with 78.9 g $(EtO)_2P(O)CH(CMe_3)N(CMe_3)O\bullet$ in PhMe in the presence of Cu, CuBr, and N,N,N',N',N''-pentamethyldiethylenetriamine and reaction of 2 g resulting monoalkoxyamine 20 h at reflux with 0.55 g 1,4-butanediol diacrylate in EtOH.

IT 850348-10-6P
(preparation of polyalkoxyamines for use as initiators in radical polymerization)

RN 850348-10-6 HCAPLUS

CN Pentanedioic acid, 4-[[[1-(diethoxyphosphinyl)-2,2-dimethylpropyl](1,1-dimethylethyl)amino]oxy]-2,2-dimethyl-, 5,5'-(1,4-butanediyl) ester (9CI) (CA INDEX NAME)



IC ICM C07F009-40

ICS C08G073-00

CC 35-4 (Chemistry of Synthetic High Polymers)

Section cross-reference(s): 29

IT 850348-10-6P

(preparation of polyalkoxyamines for use as initiators in radical polymerization)

REFERENCE COUNT:

3

THERE ARE 3 CITED REFERENCES AVAILABLE
FOR THIS RECORD. ALL CITATIONS AVAILABLE
IN THE RE FORMAT

L26 ANSWER 9 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2005:142258 HCAPLUS

DOCUMENT NUMBER: 142:374222

TITLE: Surface initiated polymerization of poly(butyl
acrylate) by nitroxide mediated
polymerization: first comparative
polymerization of a bimolecular and a
unimolecular initiator-grafted silica
particlesAUTHOR(S): Parvole, Julien; Laruelle, Gael; Khoukh,
Abdel; Billon, LaurentCORPORATE SOURCE: Laboratoire de Physico-Chimie des Polymeres,
UMR 5067 CNRS, Universite de Pau et Pays de
l'Adour Helioparc Pau-Pyrenees, Pau, 64053,
Fr.SOURCE: Macromolecular Chemistry and Physics (2005),
206(3), 372-382

CODEN: MCHPES; ISSN: 1022-1352

PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal

LANGUAGE: English

AB Hybrid silica-particles comprising an inorg. core and an organic
polymer shell were synthesized by nitroxide mediated polymerization of Bu
acrylate in the presence of a grafted alkoxyamine. The layer of
initiator mols. attached to the surface of silica is based on an
acyclic β -phosphonylated nitroxide also referred to SG1. The
synthesis and the characterization by NMR of this alkoxyamine
structure are briefly described. Moreover, the grafted initiator
particles were studied by XPS, NMR 29Si CP/MAS, and TGA to determine
the nature of the anchorage sites and the grafting d. With this
stable radical as chain growth moderator tethered to the inorg.
core, the grafting from polymerization exhibits a control character with

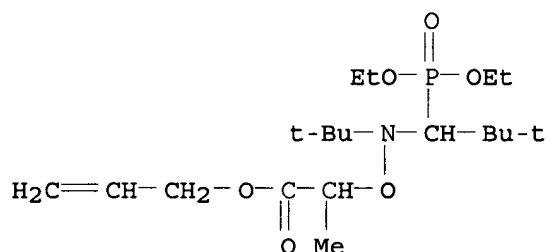
a low polydispersity index ($I < 1.1$). For the first time, a comparative study with a bimol. system based on a grafted azoic initiator in presence of SG1 is also described. A different kinetic behavior was demonstrated and interpreted in terms of variation of the initial [monomer]/[initiator] ratio.

IT 763105-79-9P

(synthesis of allyl alkoxyamine for surface initiated graft polymerization of poly(Bu acrylate) on silica particles)

RN 763105-79-9 HCAPLUS

CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, 2-propenyl ester, 6-oxide (9CI) (CA INDEX NAME)



CC 35-4 (Chemistry of Synthetic High Polymers)

Section cross-reference(s): 38

IT 763105-79-9P

(synthesis of allyl alkoxyamine for surface initiated graft polymerization of poly(Bu acrylate) on silica particles)

REFERENCE COUNT: 52 THERE ARE 52 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L26 ANSWER 10 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2004:822885 HCAPLUS

DOCUMENT NUMBER: 141:296170

TITLE: β -Phosphorylated alkoxyamines and their use in preparing α - ω functionalized monomers or polymers

INVENTOR(S): Couturier, Jean-Luc; Guerret, Olivier

PATENT ASSIGNEE(S): Atofina, Fr.

SOURCE: Eur. Pat. Appl., 15 pp.

CODEN: EPXXDW

DOCUMENT TYPE: Patent

LANGUAGE: French

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 1464648	A1	20041006	EP 2004-290777	2004 0323
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, PL, SK, HR				
FR 2853317	A1	20041008	FR 2003-3999	2003

FR 2853317	B1	20060707		0401
CA 2462923	AA	20041001	CA 2004-2462923	
				2004
				0330
US 2005065119	A1	20050324	US 2004-813822	
				2004
				0331
JP 2004307502	A2	20041104	JP 2004-109037	
				2004
				0401
CN 1576280	A	20050209	CN 2004-10038709	
				2004
				0401
PRIORITY APPLN. INFO.:		FR 2003-3999	A	
				2003
				0401

OTHER SOURCE(S): MARPAT 141:296170

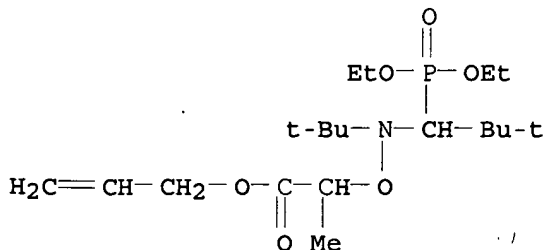
AB β -Phosphorylated alkoxyamines A-OCCMe(R)(M)nON(CMe₃)CH(CMe₃)P(O)(OEt)₂ [I; A = HO, MeO, R₁O, Cl; M₁ = Li, Na, K, H₄N⁺, Bu₄N⁺, Bu₃NH⁺; R = H, Me; R₁ = (un)branched C₁-6 alkyl; M = monomeric, vinylic chain susceptible to radical polymerization, preferably (un)substituted styrene, dienes, (meth)acrylic acids, alkyl (meth)acrylates, acrylonitrile, acrylamide derivs., vinylpyrrolidinone or a mixture of at least 2 of these; n = an integer which can be 0], preferably I (A = HO, Cl; n = 0), are claimed for use in preparation of mono- or polyalkoxyamines Z[OCCMe(R)(M)nON(CMe₃)CH(CMe₃)P(O)(OEt)₂]_x [II; same R, M, n; x \geq 1; Z = mono- or polyfunctional structure, e.g., CH₂:CHCH₂O, CH₂:CHCH₂NH, Me(OCH₂CH₂)pO, O(CH₂)qO; p, q = \geq 1], preferably II (Z = CH₂:CHCH₂O, CH₂:CHCH₂NH, n = 0, R = H, x = 1; Z = O(CH₂)₄O, n = 0, R = Me, x = 2; Z = Me(OCH₂CH₂)pO, n = 0, R = Me, x = 1). In an example, treating 5.4 mmol HO₂CCHMeON(CMe₃)CH(CMe₃)P(O)(OEt)₂ (preparation given) in 25 mL CH₂Cl₂ with 16.2 mmol SOCl₂ 45 min at room temperature gave the corresponding acid chloride, which was subsequently dissolved in 30 mL Et₂O and treated with 10.8 mmol allyl alc., 5.4 mmol Et₃N, 1.1 mmol DMAP and 10 mL Et₂O for 2 h at room temperature to afford, after workup, 60% CH₂:CHCH₂O₂CCHMeON(CMe₃)CH(CMe₃)P(O)(OEt)₂.

IT 763105-79-9P 763105-81-3P 763105-82-4P
763105-83-5P

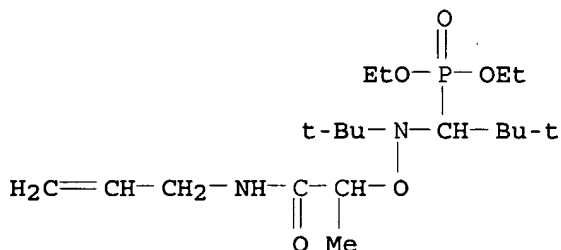
(preparation of α - ω functionalized monomers or polymers from β -phosphorylated alkoxyamines)

RN 763105-79-9 HCAPLUS

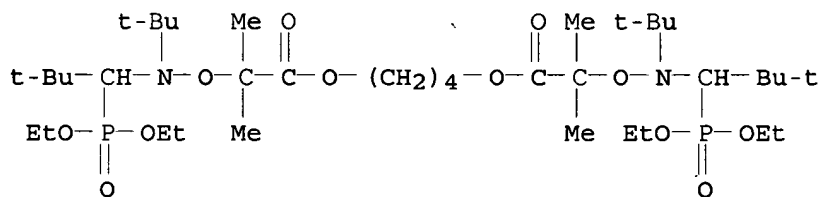
CN 3,7-Dioxa-4-aza-6-phosphanonoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, 2-propenyl ester, 6-oxide (9CI) (CA INDEX NAME)



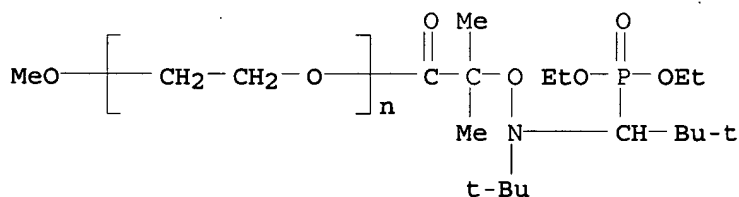
RN 763105-81-3 HCAPLUS
 CN Phosphonic acid, [1-[(1,1-dimethylethyl)[1-methyl-2-oxo-2-(2-propenylamino)ethoxy]amino]-2,2-dimethylpropyl]-, diethyl ester (9CI) (CA INDEX NAME)



RN 763105-82-4 HCAPLUS
 CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2,2-dimethyl-, 1,4-butanediyl ester, 6,6'-dioxide (9CI) (CA INDEX NAME)



RN 763105-83-5 HCAPLUS
 CN Poly(oxy-1,2-ethanediyl), α -[4,5-bis(1,1-dimethylethyl)-6-ethoxy-2,2-dimethyl-6-oxido-1-oxo-3,7-dioxa-4-aza-6-phosphanon-1-yl]- ω -methoxy- (9CI) (CA INDEX NAME)



IC ICM C07F009-40
 ICS C08F004-00
 CC 29-7 (Organometallic and Organometalloidal Compounds)
 Section cross-reference(s): 35
 IT 763105-79-9P 763105-81-3P 763105-82-4P
 763105-83-5P
 (preparation of α - ω functionalized monomers or polymers
 from β -phosphorylated alkoxyamines)

L26 ANSWER 11 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2003:591230 HCAPLUS
 DOCUMENT NUMBER: 139:134362

TITLE: Method of producing and using materials which are reinforced against impact and which contain block copolymers that are obtained by means of controlled radical polymerization in the presence of nitroxides

INVENTOR(S): Ruzette, Anne-valerie; Chauvin, Florence; Guerret, Olivier; Bertin, Denis; Vuillemin, Bruno; Leibler, Ludwik; Gerard, Pierre; Ederle, Yannick

PATENT ASSIGNEE(S): ATOFINA, Fr.

SOURCE: PCT Int. Appl., 30 pp.
CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: French

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2003062293	A1	20030731	WO 2003-FR186	2003 0121
WO 2003062293	C1	20050428		
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
CA 2473791	AA	20030731	CA 2003-2473791	2003 0121
EP 1468029	A1	20041020	EP 2003-712271	2003 0121
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK				
JP 2005515281	T2	20050526	JP 2003-562170	2003 0121
CN 1643013	A	20050720	CN 2003-805719	2003 0121
US 2006063891	A1	20060323	US 2005-502216	2005 1116
PRIORITY APPLN. INFO.:				FR 2002-814 A
				2002 0122
				FR 2002-1765 A
				2002

0213

WO 2003-FR186

W

2003

0121

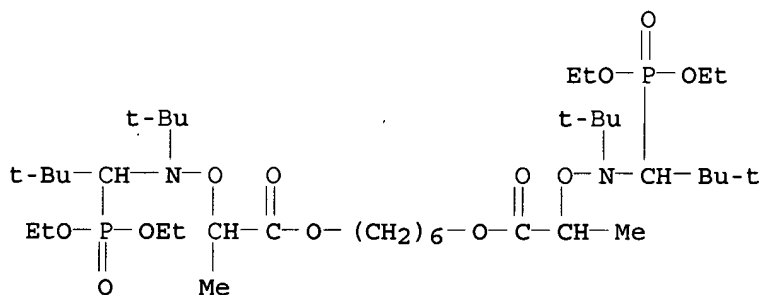
AB The invention relates to the production and use of block copolymers which are obtained by means of controlled radical polymerization in the presence of nitroxides for the purpose of reinforcing brittle polymer matrixes. The invention offers advantages such as (i) simplicity of copolymer synthesis and use and (ii) fine dispersion of the copolymer mols. in the brittle matrix, which ensures both the transparency of the material and high reinforcement against impact. More specifically, the invention relates to the radical synthesis of block copolymers comprising at least three blocks, which include one block having a glass transition temperature of less than 0°C and a thermoplastic end block having a glass transition temperature of more than 0°C, thereby guaranteeing compatibility with the brittle matrix to be reinforced against impact. A typical block copolymer was manufactured by radical polymerization of 3600 g Bu acrylate at 115° in the presence of 59.7073 g $\text{CH}_2[(\text{CH}_2)_3\text{OCOCHMeON}(\text{CMe}_3)\text{CH}(\text{CMe}_3)\text{P}(\text{:O})(\text{OEt})_2]_2$ and 3.1907 g $(\text{EtO})_2\text{P}(\text{:O})\text{CH}(\text{CMe}_3)\text{N}(\text{CMe}_3)\text{O}\bullet$, and polymerization of 6250 g Me methacrylate at 120° in the presence of 1800 g resulting intermediate polymer.

IT 300811-94-3 300811-95-4

(manufacture of block copolymer impact improvers by controlled radical polymerization in presence of nitroxides and alkoxyamines)

RN 300811-94-3 HCAPLUS

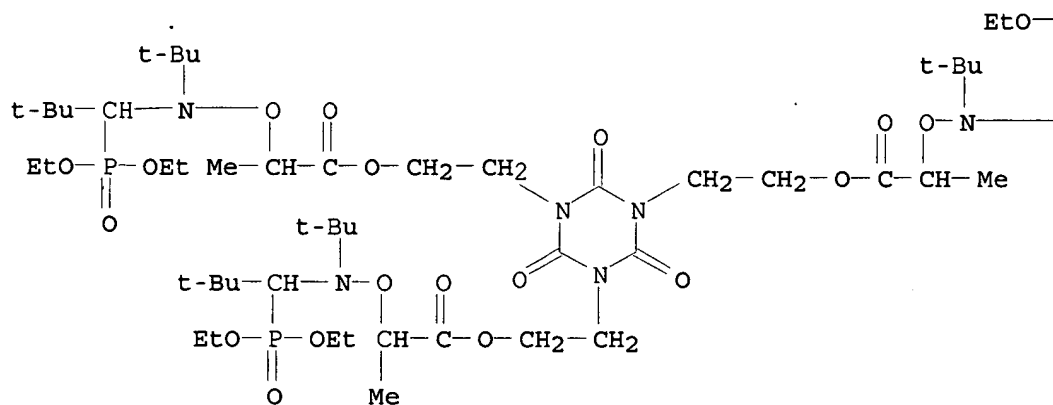
CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, 1,6-hexanediyl ester, 6,6'-dioxide (9CI) (CA INDEX NAME)



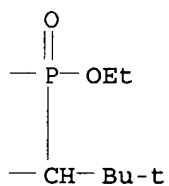
RN 300811-95-4 HCAPLUS

CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, (2,4,6-trioxo-1,3,5-triazine-1,3,5(2H,4H,6H)-triyl)tri-2,1-ethanediyl ester, 6,6',6''-trioxide (9CI) (CA INDEX NAME)

PAGE 1-A



PAGE 1-B



IC ICM C08F293-00
 ICS C08L053-00; C08L101-00
 CC 37-6 (Plastics Manufacture and Processing)
 Section cross-reference(s): 35
 IT 300811-94-3 300811-95-4
 (manufacture of block copolymer impact improvers by controlled radical polymerization in presence of nitroxides and alkoxyamines)
 REFERENCE COUNT: 7 THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L26 ANSWER 12 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2002:709890 HCAPLUS
 DOCUMENT NUMBER: 137:353388
 TITLE: Controlled/Living Radical Polymerization of tert-Butyl Acrylate Mediated by Chiral Nitroxides. A Stereochemical Study
 AUTHOR(S): Ananchenko, Gennady; Matyjaszewski, Krzysztof
 CORPORATE SOURCE: Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, 15213, USA
 SOURCE: Macromolecules (2002) 35(22), 8323-8329
 CODEN: MAMOBX; ISSN: 0024-9297
 PUBLISHER: American Chemical Society
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 AB The two diastereomeric alkoxyamines of tBP-DEPN, where tBP is 1-(tert-butoxycarbonyl)ethyl and DEPN is N-(2-methylpropyl)-N-(1-diethylphosphophono-2,2-dimethylpropyl)aminoxyl, have marked

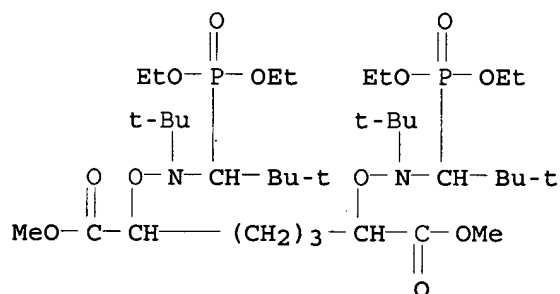
differences in their thermodyn. stability (ratio of diastereomers is 5:1 at 100° in o-dichlorobenzene). They were used as initiators for the controlled/living radical polymerization of tert-Bu acrylate to test the premise that such moderators could potentially affect the tacticity of the resulting poly(tert-Bu acrylate). 2D NMR was used to analyze the end group configuration for the samples with shorter chain lengths (DP = 15-20). Although the diastereomeric excess in the polymer alkoxyamine end group is even higher than for the model compound (ratio of diastereomers is 7:1), the distribution of terminal triads in poly(tert-Bu acrylate) does not differ from those in the entire chain and is identical to that of the polymers prepared by ATRP (atom transfer radical polymerization). Thus, the tacticities of the poly(tert-Bu acrylate)s prepared by DEPN-mediated polymerization, ATRP, and conventional free radical polymerization were the same.

IT 474832-44-5P

(initiator; preparation of chiral nitroxide initiators and stereochem. study on controlled/living radical polymerization of tert-Bu acrylate mediated by chiral nitroxides)

RN 474832-44-5 HCAPLUS

CN Heptanedioic acid, 2,6-bis[[[1-(diethoxyphosphinyl)-2,2-dimethylpropyl](1,1-dimethylethyl)amino]oxy]-, dimethyl ester (9CI) (CA INDEX NAME)



CC 35-3 (Chemistry of Synthetic High Polymers)

IT 474832-43-4P 474832-44-5P

(initiator; preparation of chiral nitroxide initiators and stereochem. study on controlled/living radical polymerization of tert-Bu acrylate mediated by chiral nitroxides)

REFERENCE COUNT: 41 THERE ARE 41 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

✓ L26 ANSWER 13 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2002:624966 HCAPLUS

DOCUMENT NUMBER: 137:353359

TITLE: Use of a difunctional alkoxyamine initiator in the miniemulsion polymerization of n-butyl acrylate

AUTHOR(S): Farcet, Celine; Charleux, Bernadette; Pirri, Rosangela; Guerret, Olivier

CORPORATE SOURCE: Lab. Chimie Macromoleculaire, UMR 760, Univ. Pierre et Marie Curie, Paris, 75252, Fr.

SOURCE: Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) (2002), 43(2), 98-99

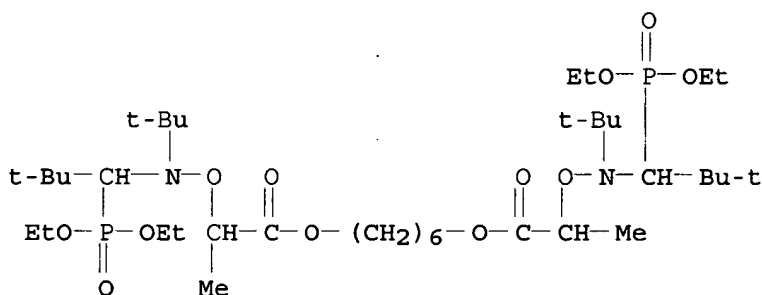
CODEN: ACPPAY; ISSN: 0032-3934
 PUBLISHER: American Chemical Society, Division of Polymer Chemistry
 DOCUMENT TYPE: Journal; (computer optical disk)
 LANGUAGE: English

AB The application of controlled free-radical polymerization to aqueous dispersed systems offers the opportunity to directly prepare well-defined copolymers in a latex form. In the presented work a SG1-based difunctional alkoxyamine was used as an initiator for the homopolymer of Bu acrylate in aqueous miniemulsion, first to increase the achievable molar mass and second, to use the polymer as a difunctional macroinitiator for the synthesis of triblock copolymers in aqueous dispersed systems. Well-defined polymers with one alkoxyamine functionality at each end were obtained, providing that monomer conversion was kept below 70%. Beyond this conversion, extensive broadening of the molar mass distribution was evidenced, as the consequence of termination and transfer to polymer. These α,ω -difunctional homopolymers were used as precursors for the synthesis of triblock copolymers.

IT 300811-94-3
 (difunctional alkoxyamine initiator in miniemulsion polymerization of Bu acrylate)

RN 300811-94-3 HCAPLUS

CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, 1,6-hexanediyl ester, 6,6'-dioxide (9CI) (CA INDEX NAME)



CC 35-3 (Chemistry of Synthetic High Polymers)

IT 300811-94-3
 (difunctional alkoxyamine initiator in miniemulsion polymerization of Bu acrylate)

REFERENCE COUNT: 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L26 ANSWER 14 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2002:319042 HCAPLUS

DOCUMENT NUMBER: 137:20639

TITLE: Synthesis and Characterization of Poly(styrene-b-n-butyl acrylate-b-styrene) Triblock Copolymers Using a Dialkoxyamine as Initiator

AUTHOR(S): Robin, Sophie; Guerret, Olivier; Couturier, Jean-Luc; Pirri, Rosangela; Gnanou, Yves

CORPORATE SOURCE: Laboratoire de Chimie des Polymeres Organiques, ENSCPB-CNRS-Universite Bordeaux 1,

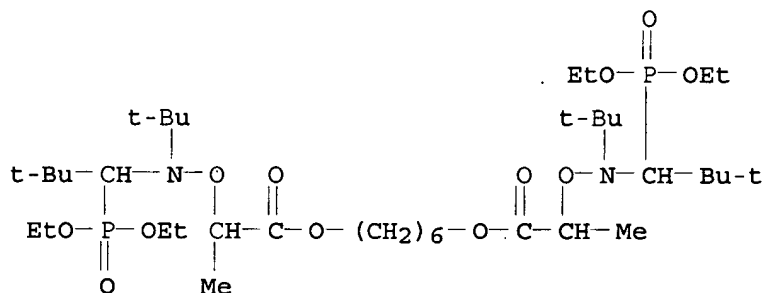
SOURCE: Talence, 33402, Fr.
 Macromolecules (2002), 35(10), 3844-3848
 CODEN: MAMOBX; ISSN: 0024-9297
 PUBLISHER: American Chemical Society
 DOCUMENT TYPE: Journal
 LANGUAGE: English

AB This study investigates the ability of a novel difunctional alkoxyamine based on N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (SG1) to serve as initiator for the controlled radical polymerization of styrene (S) and Bu acrylate (nBuA). The efficiency of this initiator was checked using three different methods. After we set up the conditions best suited to the synthesis of perfectly difunctional poly(Bu acrylate) (PnBuA) samples, well-defined poly(styrene-b-Bu acrylate-b-styrene) triblock copolymers could be obtained by sequential polymerization of the corresponding monomers. However, a loss of control of the targeted structure was observed whenever the conversion of styrene exceeded 40%.

IT 300811-94-3
 (initiators; preparation and characterization of Bu acrylate-styrene triblock copolymers using dialkoxyamine as initiator)

RN 300811-94-3 HCAPLUS

CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, 1,6-hexanediyl ester, 6,6'-dioxide (9CI) (CA INDEX NAME)



CC 35-3 (Chemistry of Synthetic High Polymers)

IT 300811-94-3
 (initiators; preparation and characterization of Bu acrylate-styrene triblock copolymers using dialkoxyamine as initiator)

REFERENCE COUNT: 21 THERE ARE 21 CITED REFERENCES AVAILABLE
 FOR THIS RECORD. ALL CITATIONS AVAILABLE
 IN THE RE FORMAT

L26 ANSWER 15 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2002:151910 HCAPLUS

DOCUMENT NUMBER: 136:325922

TITLE: Synthesis of Stars and Starlike Block
 Copolymers from a Trialkoxyamine Used as
 Initiator

AUTHOR(S): Robin, Sophie; Guerret, Olivier; Couturier,
 Jean-Luc; Gnanou, Yves

CORPORATE SOURCE: Laboratoire de Chimie des Polymeres
 Organiques, ENSCPB-CNRS-Universite Bordeaux-I,
 Talence, 33402, Fr.

SOURCE: Macromolecules (2002), 35(7), 2481-2486

PUBLISHER: CODEN: MAMOBX; ISSN: 0024-9297
 DOCUMENT TYPE: American Chemical Society
 LANGUAGE: Journal
 English

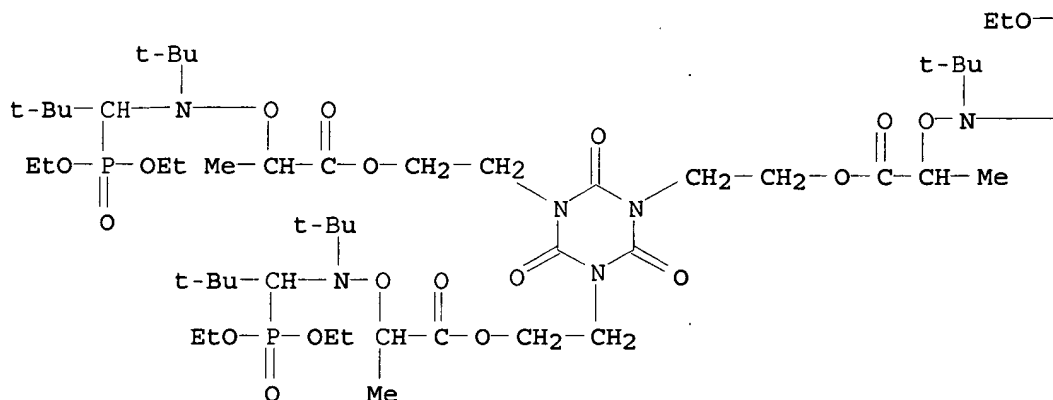
AB This study investigates the efficiency of a novel trifunctional alkoxyamine (1) based on N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (SG1) (2) as initiator for the controlled radical polymerization of styrene (S) and Bu acrylate (nBuA). Three factors, namely the concentration of SG1 initially introduced in excess, the monomer conversion, and-in the specific case of PS samples-the monomer autopolymer., were found to control the quality of the star samples obtained. Well-defined T-(PBuA-b-PS)₃ star block copolymers could also be synthesized by sequential copolymer. using the same trifunctional initiator.

IT 300811-95-4P
 (catalyst; in synthesis of stars and starlike block copolymers from a trialkoxyamine used as initiator)

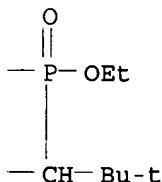
RN 300811-95-4 HCAPLUS

CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, (2,4,6-trioxo-1,3,5-triazine-1,3,5(2H,4H,6H)-triyl)tri-2,1-ethanediyl ester, 6,6',6''-trioxide (9CI) (CA INDEX NAME)

PAGE 1-A



PAGE 1-B



CC 35-4 (Chemistry of Synthetic High Polymers)

IT 300811-95-4P

(catalyst; in synthesis of stars and starlike block copolymers from a trialkoxyamine used as initiator)

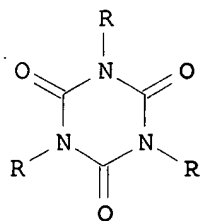
REFERENCE COUNT: 26 THERE ARE 26 CITED REFERENCES AVAILABLE

FOR THIS RECORD. ALL CITATIONS AVAILABLE
IN THE RE FORMAT

L26 ANSWER 16 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2001:747176 HCAPLUS
 DOCUMENT NUMBER: 135:289208
 TITLE: Multimodal polymers by controlled radical
 polymerization in the presence of alkoxyamines
 Guerret, Olivier; Robin, Sophie; Gnanou, Yves
 INVENTOR(S): ATOFINA, Fr.
 PATENT ASSIGNEE(S):
 SOURCE: Eur. Pat. Appl., 24 pp.
 CODEN: EPXXDW
 DOCUMENT TYPE: Patent
 LANGUAGE: French
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 1142913	A1	20011010	EP 2001-106802	2001 0319
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO				
FR 2807439	A1	20011012	FR 2000-4557	2000 0407
FR 2807439	B1	20030613		
CA 2343339	AA	20011007	CA 2001-2343339	2001 0406
CA 2343339	C	20011007		
CN 1318570	A	20011024	CN 2001-117832	2001 0407
JP 2001316409	A2	20011113	JP 2001-109720	2001 0409
US 2002040117	A1	20020404	US 2001-828476	2001 0409
US 6646079	B2	20031111		
PRIORITY APPLN. INFO.:			FR 2000-4557	A 2000 0407

GI



I, R = (CH₂)₂O₂CCHMeON(CMe₃)CH(CMe₃)P(O)(OEt)₂

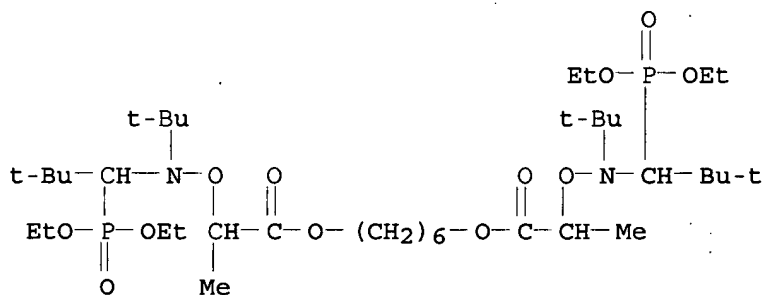
AB Polymers with multimodal d.p. are manufactured by radical polymerization of monomers in the presence of alkoxyamines having ≥1 amine group and groups with mol. weight >15 in the β-position to the N, such as triazine derivative I.

IT 300811-94-3 300811-95-4

(multimodal polymers by controlled radical polymerization in presence of alkoxyamines)

RN 300811-94-3 HCAPLUS

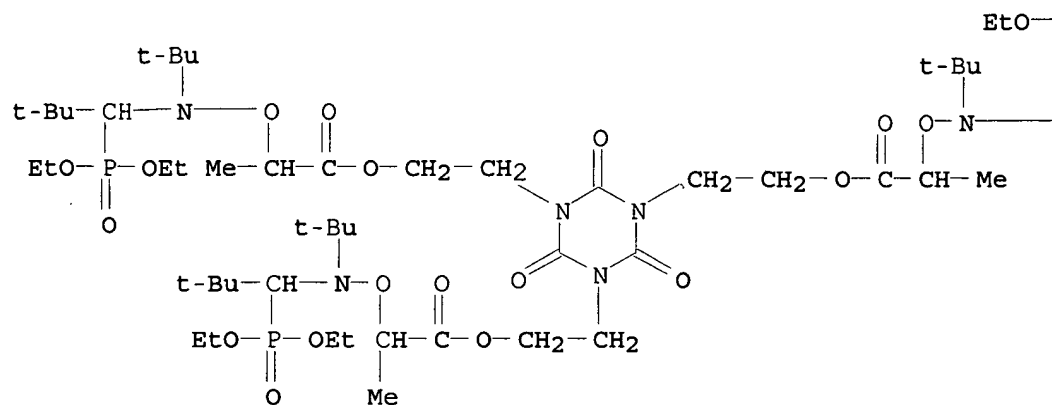
CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, 1,6-hexanediyl ester, 6,6'-dioxide (9CI) (CA INDEX NAME)



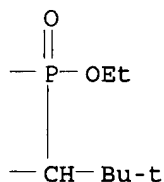
RN 300811-95-4 HCAPLUS

CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, (2,4,6-trioxo-1,3,5-triazine-1,3,5(2H,4H,6H)-triyl)tri-2,1-ethanediyl ester, 6,6',6''-trioxide (9CI) (CA INDEX NAME)

PAGE 1-A



PAGE 1-B



IC ICM C08F004-00
 ICS C08F293-00; C08F002-38
 CC 35-4 (Chemistry of Synthetic High Polymers)
 IT 78-67-1, Azobisisobutyronitrile 300811-93-2 300811-94-3
 300811-95-4 364731-73-7
 (multimodal polymers by controlled radical polymerization in presence
 of alkoxyamines)

REFERENCE COUNT: 7 THERE ARE 7 CITED REFERENCES AVAILABLE
 FOR THIS RECORD. ALL CITATIONS AVAILABLE
 IN THE RE FORMAT

L26 ANSWER 17 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2001:31452 HCAPLUS

DOCUMENT NUMBER: 134:101275

TITLE: Preparation of mono and multifunctional
 alkoxyamines for forming nitroxyl radical
 initiators and regulators useful in the
 preparation of polymers with narrow
 polydispersity

INVENTOR(S): Kramer, Andreas; Nesvadba, Peter; Zink,
 Marie-Odile; Wunderlich, Wiebke

PATENT ASSIGNEE(S): Ciba Specialty Chemicals Holding Inc., Switz.

SOURCE: PCT Int. Appl., 74 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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WO 2001002345	A2	20010111	WO 2000-EP5899	2000 0626
WO 2001002345	A3	20010719		
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RW:			GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG	
CA 2375806	AA	20010111	CA 2000-2375806	2000 0626
EP 1189875	A2	20020327	EP 2000-951302	2000 0626
EP 1189875	B1	20040804		
R:			AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, MC, PT, IE, SI, LT, LV, FI, RO	
JP 2003503474	T2	20030128	JP 2001-507787	2000 0626
AT 272610	E	20040815	AT 2000-951302	2000 0626
US 6875831	B1	20050405	US 2001-19618	2001 1220
PRIORITY APPLN. INFO.:			EP 1999-810567	A 1999 0702
			WO 2000-EP5899	W 2000 0626

OTHER SOURCE(S): MARPAT 134:101275

AB The title alkoxyamines especially useful for the living polymerization of unsatd. monomers or/and oligomers giving polymers with good conversion are compds. bearing groups which can liberate stable free nitroxyl radicals of specific structures.

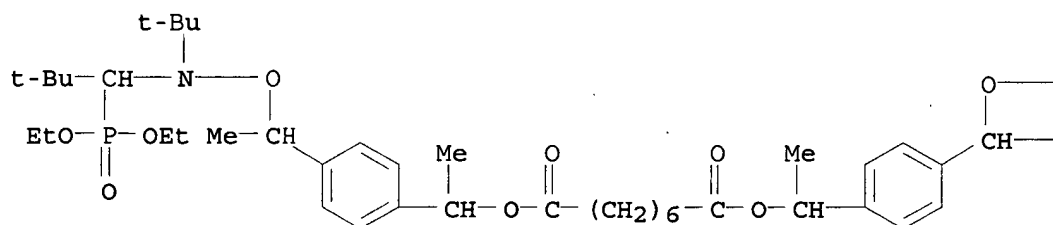
IT 319458-54-3P

(initiator; preparation of mono and multifunctional alkoxyamines as initiators for free radical polymerization with narrow polydispersity)

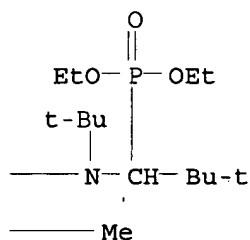
RN 319458-54-3 HCAPLUS

CN Octanedioic acid, bis[1-[4-[3,4-bis(1,1-dimethylethyl)-5-ethoxy-1-methyl-5-oxido-2,6-dioxa-3-aza-5-phosphaoct-1-yl]phenyl]ethyl] ester (9CI) (CA INDEX NAME)

PAGE 1-A



PAGE 1-B



IC ICM C07C239-20
ICS C07D211-94; C08F004-00
CC 35-3 (Chemistry of Synthetic High Polymers)
IT 264280-51-5P 319457-98-2P 319457-99-3P 319458-00-9P
319458-01-0P 319458-02-1P 319458-03-2P 319458-05-4P
319458-06-5P 319458-07-6P 319458-09-8P 319458-10-1P
319458-13-4P 319458-14-5P 319458-18-9P 319458-19-0P
319458-20-3P 319458-21-4P 319458-22-5P 319458-23-6P
319458-24-7P 319458-27-0P 319458-29-2P 319458-32-7P
319458-34-9P 319458-37-2P 319458-40-7P 319458-43-0P
319458-46-3P 319458-49-6P 319458-51-0P **319458-54-3P**
(initiator; preparation of mono and multifunctional alkoxyamines as
initiators for free radical polymerization with narrow polydispersity)

L26 ANSWER 18 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2000:842098 HCAPLUS

DOCUMENT NUMBER: 134:29789

TITLE: Alkoxyamine phosphonates and their use as
polymerization catalysts

INVENTOR(S): Guerret, Olivier; Couturier, Jean-Luc; Lutz,
Jean-Francois; Le Mercier, Christophe; Robin,
Sophie; Vuillemin, Bruno

PATENT ASSIGNEE(S): ATOFINA, Fr.

SOURCE: PCT Int. Appl., 59 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: French

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.

KIND

DATE

APPLICATION NO.

DATE

 WO 2000071501 A1 20001130 WO 2000-FR1287

2000
0512

W: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN,
 CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM,
 HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,
 LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ,
 PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT,
 TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ,
 MD, RU, TJ, TM

RW: GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH,
 CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT,
 SE, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN,
 TD, TG

FR 2794459 A1 20001208 FR 1999-6329

1999
0519

FR 2794459 B1 20040903

EP 1178955 A1 20020213 EP 2000-929608

2000
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R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE,
 MC, PT, IE, SI, LT, LV, FI, RO

JP 2003500378 T2 20030107 JP 2000-619758

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US 6657043 B1 20031202 US 2002-979124

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PRIORITY APPLN. INFO.:

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A

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WO 2000-FR1287

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2000
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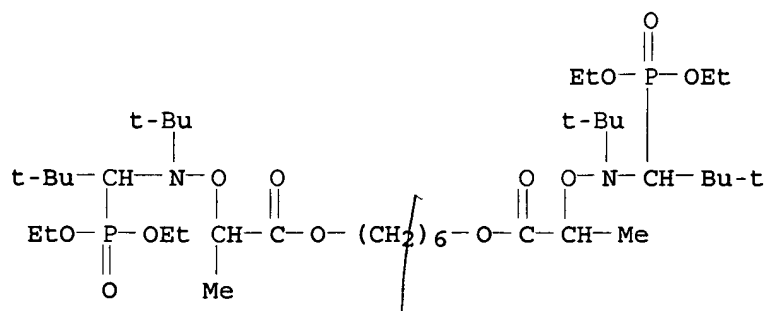
AB Alkoxyamine phosphonates containing 2-3 alkoxyamine groups are
 obtained from β -substituted nitroxides such as di-Et
 2,2-dimethyl-1-(tert-butylamino)propylphosphonate N-oxide (I) and
 are suitable for application as radical polymerization catalysts with
 good control. The inventive compds. can be used as initiators for
 (co)polymns. of at least one radically polymerizable monomer.
 Thus, I was condensed (2:1) with the Br groups in 1,6-hexanediol
 bis(2-bromopropionate) to give a bis(alkoxyamine phosphonate)
 which could be used to homopolymerize styrene or block
 copolymerize styrene with Bu acrylate.

IT 300811-94-3P 300811-95-4P 310878-79-6P
 310878-80-9P 310878-81-0P 310878-82-1P
 310878-83-2P

(production of alkoxyamine phosphonates for use as radical polymerization
 catalysts)

RN 300811-94-3 HCAPLUS

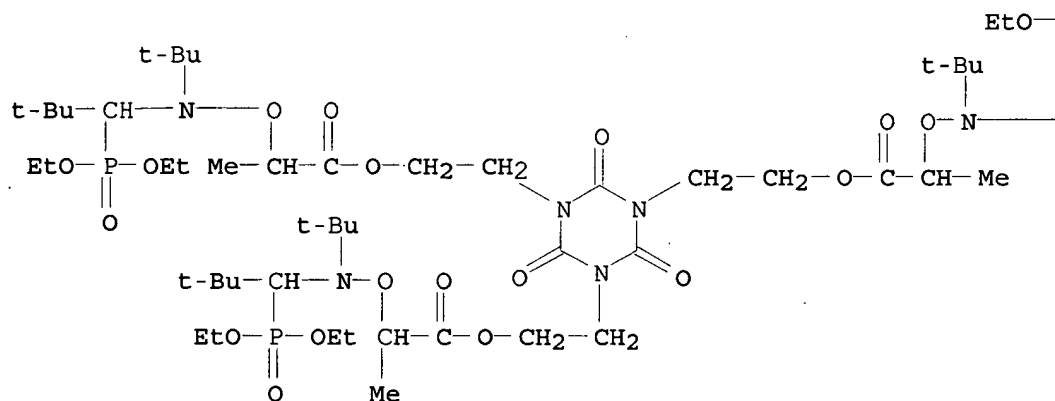
CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-
 6-ethoxy-2-methyl-, 1,6-hexanediyl ester, 6,6'-dioxide (9CI) (CA
 INDEX NAME)



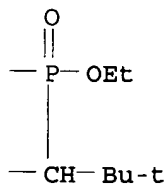
RN 300811-95-4 HCAPLUS

CN 3,7-Dioxa-4-aza-6-phosphanonoic acid, 4,5-bis(1,1-dimethylethyl)-
6-ethoxy-2-methyl-, (2,4,6-trioxo-1,3,5-triazine-1,3,5(2H,4H,6H)-
triy1)tri-2,1-ethanediyl ester, 6,6',6''-trioxide (9CI) (CA INDEX
NAME)

PAGE 1-A

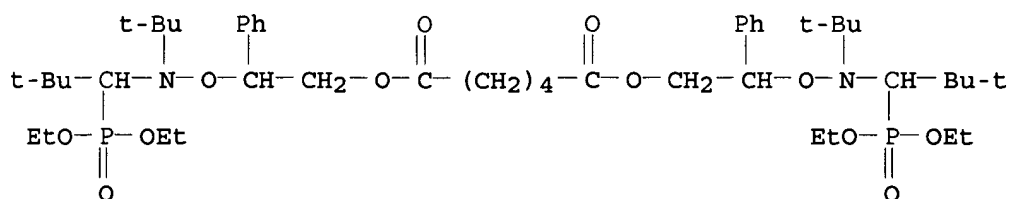


PAGE 1-B



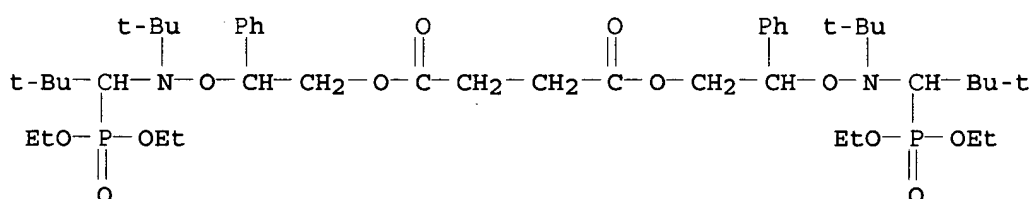
RN 310878-79-6 HCAPLUS

CN Hexanedioic acid, bis[4,5-bis(1,1-dimethylethyl)-6-ethoxy-6-oxido-2-phenyl-3,7-dioxa-4-aza-6-phosphanon-1-yl] ester (9CI) (CA INDEX NAME)



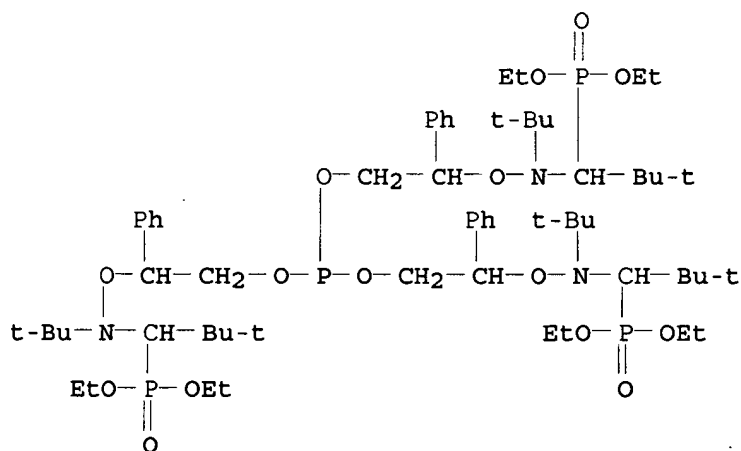
RN 310878-80-9 HCAPLUS

CN Butanedioic acid, bis[4,5-bis(1,1-dimethylethyl)-6-ethoxy-6-oxido-2-phenyl-3,7-dioxa-4-aza-6-phosphanon-1-yl] ester (9CI) (CA INDEX NAME)



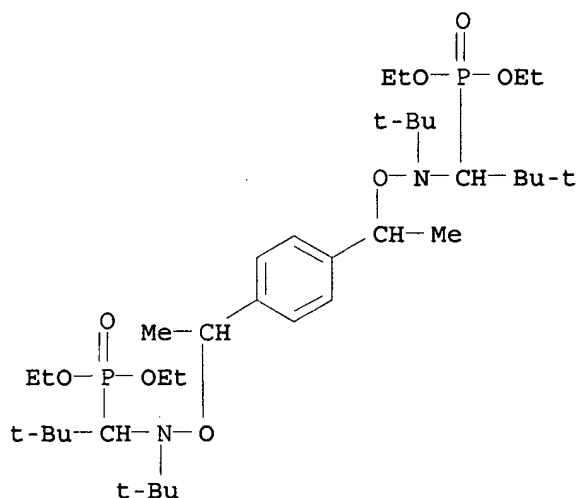
RN 310878-81-0 HCAPLUS

CN Phosphonic acid, [phosphinidynetris[oxy(1-phenyl-2,1-ethanediyl)oxy[(1,1-dimethylethyl)imino](2,2-dimethylpropylidene)]]tris-, hexaethyl ester (9CI) (CA INDEX NAME)

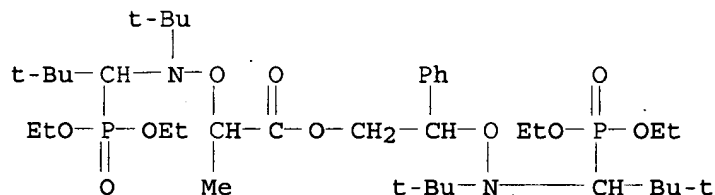


RN 310878-82-1 HCAPLUS

CN Phosphonic acid, [1,4-phenylenebis[ethylideneoxy[(1,1-dimethylethyl)imino](2,2-dimethylpropylidene)]]bis-, tetraethyl ester (9CI) (CA INDEX NAME)



RN 310878-83-2 HCAPLUS
 CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-6-oxido-2-phenyl-3,7-dioxa-4-aza-6-phosphanon-1-yl ester, 6-oxide (9CI) (CA INDEX NAME)



IC ICM C07C239-20
 ICS C07F009-40; C07D251-32; C08F004-00
 CC 35-3 (Chemistry of Synthetic High Polymers)
 Section cross-reference(s): 29
 IT 300811-94-3P 300811-95-4P 310878-79-6P
 310878-80-9P 310878-81-0P 310878-82-1P
 310878-83-2P
 (production of alkoxyamine phosphonates for use as radical polymerization catalysts)

REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L26 ANSWER 19 OF 19 HCAPLUS COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 2000:593981 HCAPLUS
 DOCUMENT NUMBER: 133:297016
 TITLE: Macromolecular engineering using novel alkoxyamines
 AUTHOR(S): Granou, Yves; Robin, Sophie; Guerrer, O.; Couturier, J. L.
 CORPORATE SOURCE: Laboratoire de Chimie des Polymeres Organiques, ENSCPB-CNRS-Universite Bordeaux 1 (UMR 5629), Talence, 33402, Fr.

SOURCE: Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) (2000), 41(2), 1352-1353
CODEN: ACPPAY; ISSN: 0032-3934

PUBLISHER: American Chemical Society, Division of Polymer Chemistry

DOCUMENT TYPE: Journal

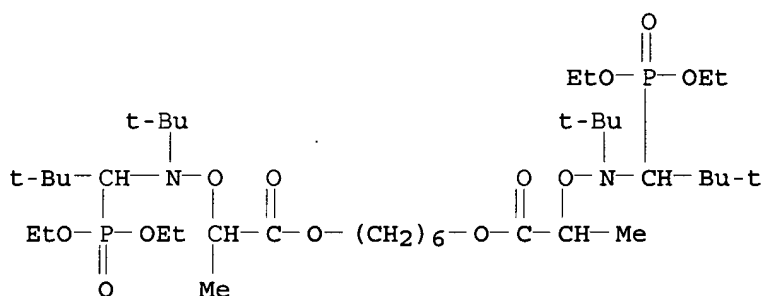
LANGUAGE: English

AB Mono, di, and trifunctional alkoxyamines based on N-tert-butyl-N-(1-diethylphosphono-2,2-dimethyl)propyl nitroxide were used to polymerize styrene and Bu acrylate, affording well-defined of linear and star structures. Triblock as well as star block copolymers constituted of poly(Bu acrylate) inner part and polystyrene outer shell were subsequently synthesized by sequentially polymerization of these two monomers, using dialkoxyamine and trialkoxyamine as initiators.

IT 300811-94-3 300811-95-4
(catalysts; polymerization of styrene and Bu acrylate in presence of alkoxyamine catalysts)

RN 300811-94-3 HCAPLUS

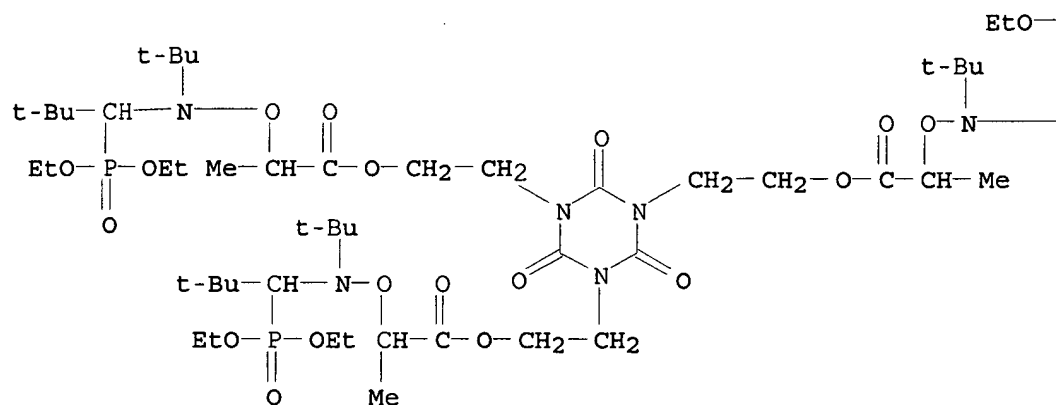
CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, 1,6-hexanediyl ester, 6,6'-dioxide (9CI) (CA INDEX NAME)



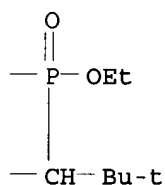
RN 300811-95-4 HCAPLUS

CN 3,7-Dioxa-4-aza-6-phosphanonanoic acid, 4,5-bis(1,1-dimethylethyl)-6-ethoxy-2-methyl-, (2,4,6-trioxo-1,3,5-triazine-1,3,5(2H,4H,6H)-triyl)tri-2,1-ethanediyl ester, 6,6',6''-trioxide (9CI) (CA INDEX NAME)

PAGE 1-A



PAGE 1-B



CC 37-3 (Plastics Manufacture and Processing)

IT 300811-93-2 300811-94-3 300811-95-4

(catalysts; polymerization of styrene and Bu acrylate in presence of alkoxyamine catalysts)

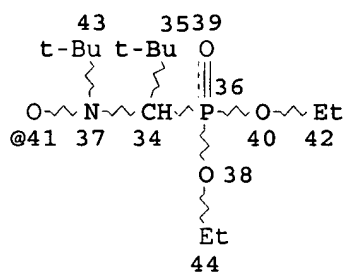
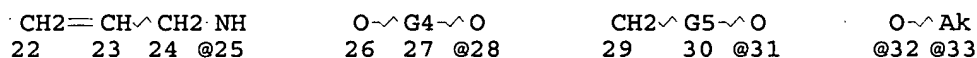
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FOR THIS RECORD. ALL CITATIONS AVAILABLE
IN THE RE FORMAT

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REP G5=(1-5) 32-29 33-31
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DEFAULT ELEVEL IS LIMITED
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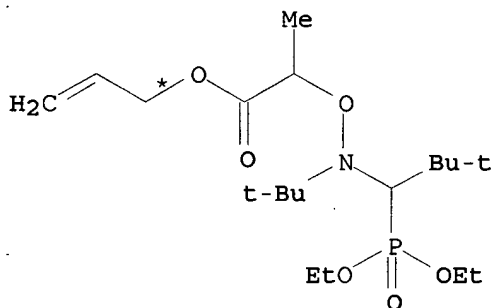
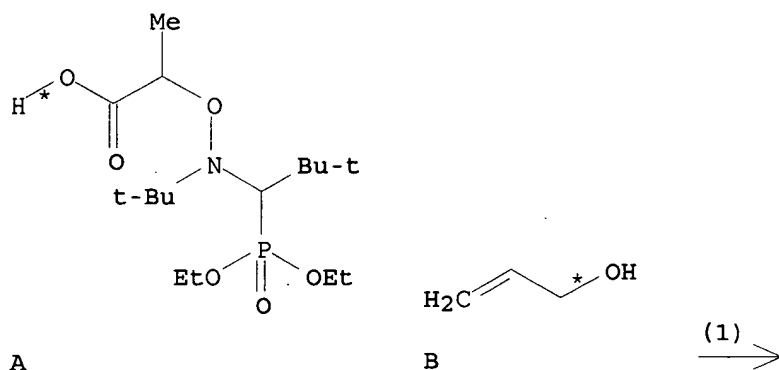
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L29 ANSWER 1 OF 8 CASREACT COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 143:347038 CASREACT
TITLE: SG1 based alkoxyamines as radical initiators
for the synthesis of lactones and lactams
AUTHOR(S): Bertin, Denis; Gimes, Didier; Marque, Sylvain
R. A.; Tordo, Paul
CORPORATE SOURCE: UMR 6517, Universites d'Aix-Marseille I, II et
III-CNRS, Marseille, 13397, Fr.
SOURCE: Tetrahedron (2005), 61(36), 8752-8761
CODEN: TETRAB; ISSN: 0040-4020
PUBLISHER: Elsevier B.V.
DOCUMENT TYPE: Journal

LANGUAGE: English

AB Recently, it has been shown that alkoxy amine derivs. can be used as radical initiators in tin-free radical chemical. Thus, a method for the preparation of highly valuable alkoxyamines was developed, which involved ionic chemical and wherein a radical cyclization was triggered by thermal initiation. Following that procedure, bicyclic, spiro and eight-membered lactones were easily prepared in good yields with very high stereoselectivity. The reaction mechanism was discussed.

RX(1) OF 26 ...A + B ==> C...



C
YIELD 40%

RX(1) RCT A 540770-92-1

STAGE(1)

SOL 75-09-2 CH₂Cl₂

CON 10 hours, reflux

STAGE(2)

RGT D 7719-09-7 SOCl₂

CON 45 minutes, room temperature

STAGE(3)

RCT B 107-18-6

RGT E 121-44-8 Et₃N, F 1122-58-3 4-DMAP

CON 16 hours, room temperature

PRO C 763105-79-9

REFERENCE COUNT: 48 THERE ARE 48 CITED REFERENCES AVAILABLE
FOR THIS RECORD. ALL CITATIONS AVAILABLE
IN THE RE FORMAT

L29 ANSWER 2 OF 8 CASREACT COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 143:26936 CASREACT

TITLE: Long-range polar effect on the C-ON bond
homolysis in (tert-butyl[1-(diethylphosphonyl)-
2,2-dimethylpropyl]-aminoxyl) SG1-based
alkoxyamines

AUTHOR(S): Bertin, Denis; Gimes, Didier; Marque, Sylvain
R. A.; Milardo, Stephan; Peri, Jerome; Tordo,
Paul

CORPORATE SOURCE: Universite de Provence, UMR 6517, Marseille,
13397/20, Fr.

SOURCE: Collection of Czechoslovak Chemical
Communications (2004), 69(12), 2223-2238
CODEN: CCCCAK; ISSN: 0010-0765

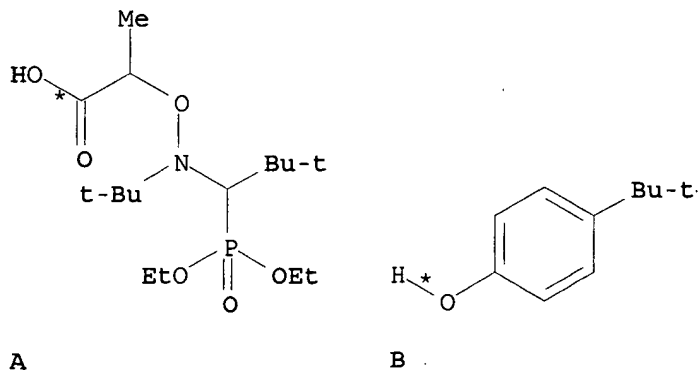
PUBLISHER: Institute of Organic Chemistry and
Biochemistry, Academy of Sciences of the Czech
Republic

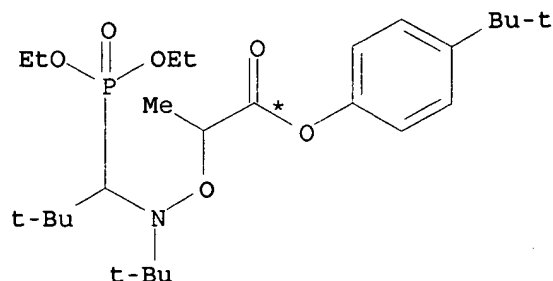
DOCUMENT TYPE: Journal

LANGUAGE: English

AB Alkoxyamines and persistent nitroxyl radicals are important
regulators of nitroxide-mediated radical polymerization. Because the
polymerization times decrease with the increasing rate constant of the
homolysis of the C-ON bond between the polymer chain and the
nitroxyl moiety, the factors influencing the cleavage rate constant
are of considerable interest. Because alkyl acrylate monomers are
among the most used in polymerization, we present the measures of the
rate consts. (kd) of the C-ON bond cleavage for new SG1 based
alkoxyamine models containing para-substituted aromatic acrylates
(4-XC6H4OC(O)C(Me)H-SG1). It appears that the values of kd
increase with the electron-withdrawing properties of the
para-substituent groups (4-X) of the ester SG1-based alkoxyamines.

RX(1) OF 7 A + B ==> C





C
YIELD 43%

RX(1) RCT A 540770-92-1

STAGE(1)

RGT D 7719-09-7 SOCl₂
SOL 75-09-2 CH₂Cl₂
CON 45 minutes, room temperature

STAGE(2)

RCT B 98-54-4
RGT E 121-44-8 Et₃N
CAT 1122-58-3 4-DMAP
SOL 60-29-7 Et₂O
CON 4 hours, room temperature

PRO C 852920-85-5

REFERENCE COUNT: 72 THERE ARE 72 CITED REFERENCES AVAILABLE
FOR THIS RECORD. ALL CITATIONS AVAILABLE
IN THE RE FORMAT

L29 ANSWER 3 OF 8 CASREACT COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 142:261127 CASREACT

TITLE: Polar, Steric, and Stabilization Effects in
Alkoxyamines C-ON Bond Homolysis: A
Multiparameter Analysis

AUTHOR(S): Bertin, Denis; Gimes, Didier; Marque, Sylvain
R. A.; Tordo, Paul

CORPORATE SOURCE: UMR 6517 Chimie Biologie et Radicaux Libres,
Universite de Provence, Marseille, 13397, Fr.

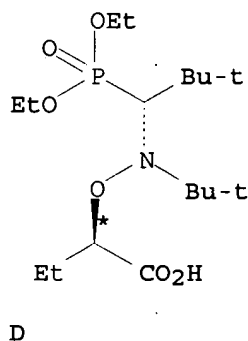
SOURCE: Macromolecules (2005), 38(7), 2638-2650
CODEN: MAMOBX; ISSN: 0024-9297

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

AB We present measurements of the rate consts. (kd) of the C-ON bond cleavage in new alkoxyamine models containing the N-(2-methyl-2-propyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-N-oxyl (SG1) moiety. The homolysis rate consts. of 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO)- and SG1-based alkoxyamines are analyzed in terms of polar inductive/field (σ_U), steric (σ), and radical stabilization (σ_{RS}) contributions of the leaving alkyl radicals, using a multiparameter equation, i.e., $\log(k_d/k_{d,0}) = \rho_U\sigma_U + \delta\sigma + \rho_{RS}\sigma_{RS}$. The rate consts. increase with increasing

$$\text{RX (1) OF 2} \quad 2 \text{ A} + 2 \text{ B} \implies \text{C} + \text{D}$$


RX (1) RCT A 188526-94-5, B 80-58-0
RGT E 3030-47-5 PMDETA
PRO C 845738-91-2, D 845738-92-3
CAT 7440-50-8 Cu, 7787-70-4 CuBr
SOL 71-43-2 Benzene
CON 3 hours, room temperature
NTE 70% overall yield

L29 ANSWER 4 OF 8 CASREACT COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 141:260134 CASREACT
TITLE: Stereochemical Studies of Chiral Acyclic
Nitroxides Coupling with a Prochiral Radical
AUTHOR(S): Braslau, Rebecca; Chaplinski, Vladimir;

CORPORATE SOURCE: Nilsen, Aaron; Arulsamy, Navamoney
 Department of Chemistry and Biochemistry,
 University of California, Santa Cruz, CA,
 95064, USA

SOURCE: Synthetic Communications (2004), 34(13),
 2433-2442
 CODEN: SYNCAV; ISSN: 0039-7911

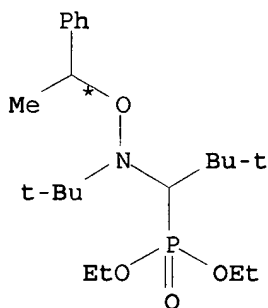
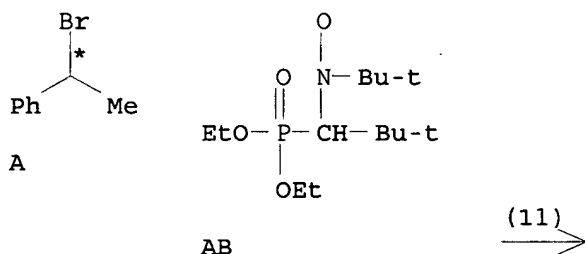
PUBLISHER: Marcel Dekker, Inc.

DOCUMENT TYPE: Journal

LANGUAGE: English

AB Acyclic chiral nitroxides bearing a hydrogen atom on the carbon adjacent to the nitroxide nitrogen were studied for stereoselectivity in a coupling reaction with the prochiral radical 1-phenethyl. In one case, an x-ray structure of the major diastereomer was obtained, which corroborates a model for predicting the stereoselectivity.

RX(11) OF 16 A + AB ==> AC



AC
 YIELD 42%

RX(11) RCT A 585-71-7

STAGE(1)

RGT E 302-01-2 N2H4
 CON 30 minutes, room temperature

STAGE(2)

RCT AB 188526-94-5
 RGT F 1309-60-0 PbO2
 SOL 108-88-3 PhMe
 CON SUBSTAGE(1) 5 minutes, room temperature

SUBSTAGE(2) room temperature -> -78 deg C
 SUBSTAGE(3) -78 deg C -> room temperature

PRO AC 224575-62-6

NTE ultrasound, stereoselective

REFERENCE COUNT: 14 THERE ARE 14 CITED REFERENCES AVAILABLE
 FOR THIS RECORD. ALL CITATIONS AVAILABLE
 IN THE RE FORMAT

L29 ANSWER 5 OF 8 CASREACT COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 141:6742 CASREACT

TITLE: Diastereomeric excess upon cleavage and
 reformation of diastereomeric alkoxyamines

AUTHOR(S): Ananchenko, Gennady; Marque, Sylvain; Gigmes,
 Didier; Bertin, Denis; Tordo, Paul

CORPORATE SOURCE: Physikalisches-Chemisches Institut, Universitaet
 Zuerich, Zurich, 8057, Switz.

SOURCE: Organic & Biomolecular Chemistry (2004), 2(5),
 709-715

CODEN: OBCRAK; ISSN: 1477-0520

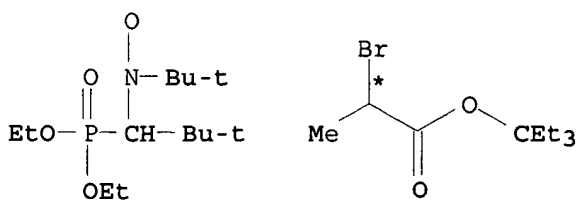
PUBLISHER: Royal Society of Chemistry

DOCUMENT TYPE: Journal

LANGUAGE: English

AB The thermal reactions of several TEMPO and DEPN
 (N-(2-methylpropan-2-yl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-
 aminoxyl) based alkoxyamines were studied by means of 1H and 31P
 NMR spectroscopy aiming to distinguish the contributions of
 diastereoselective homolysis and coupling to the total equilibrium
 diastereomeric distribution. The TEMPO-based compds. reveal no
 diastereomeric excess while DEPN based compds. show a moderate
 excess both upon homolysis and coupling. The diastereomeric
 preference of homolysis for DEPN-(propionate-like) adducts does
 not depend on the ester group and it is mainly affected by the
 size of β -substituents. The diastereoselective coupling is
 sensitive to the total recombination rate constant k_c and
 diastereoselectivity increases with the decrease of k_c . Small
 diastereoselective coupling is found in the recombination of DEPN
 with sec-Bu isobutyrate radical, where no prochiral centers are
 formed upon cleavage of corresponding alkoxyamine.

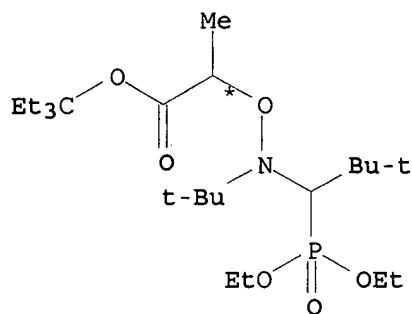
RX(3) OF 8 ...K + L ==> M



K

L





M
YIELD 97%

RX(3) RCT K 188526-94-5

STAGE(1)

RGT F 3030-47-5 PMDETA, G 7787-70-4 CuBr, H 7440-50-8
Cu
SOL 67-64-1 Me2CO
CON room temperature

STAGE(2)

RCT L 736137-70-5
CON 18 hours, 50 - 55 deg C

PRO M 695230-19-4

NTE stereoselective

REFERENCE COUNT: 53 THERE ARE 53 CITED REFERENCES AVAILABLE
FOR THIS RECORD. ALL CITATIONS AVAILABLE
IN THE RE FORMAT

L29 ANSWER 6 OF 8 CASREACT COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 140:111235 CASREACT

TITLE: Alkoxyamine-Mediated Radical Synthesis of
Indolinones and Indolines

AUTHOR(S): Leroi, Corinne; Bertin, Denis; Dufils,
Pierre-Emmanuel; Gimes, Didier; Marque,
Sylvain; Tordo, Paul; Couturier, Jean-Luc;
Guerret, Olivier; Ciufolini, Marco A.

CORPORATE SOURCE: CNRS UMR 5622, Universite Claude Bernard Lyon
1 and Ecole Superieure de Chimie Physique
Electronique de Lyon, Villeurbanne, 69622, Fr.

SOURCE: Organic Letters (2003), 5(26), 4943-4945
CODEN: ORLEF7; ISSN: 1523-7060

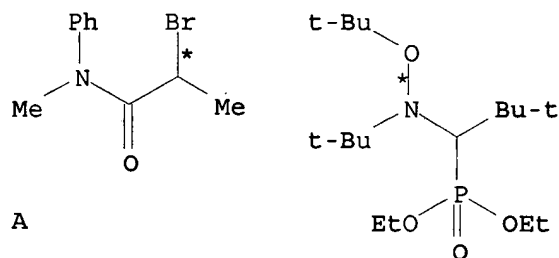
PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

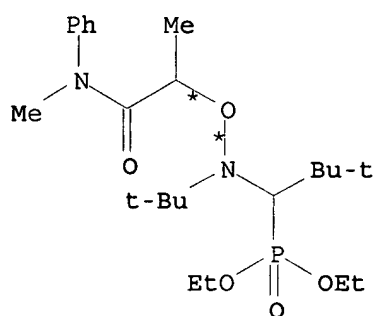
LANGUAGE: English

AB Thermolysis of α -alkoxyamino propionanilides produces
indolinones, whereas thermal reaction of N-allylaniline derivs.
with various Tordo-type alkoxyamines results in formation of
indolines in the radical regime.

RX(1) OF 67 ...A + B ==> C...



(1) →



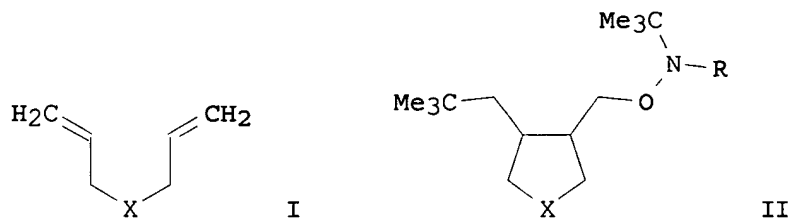
C

YIELD 90%

RX(1) RCT A 2620-11-3, B 462104-38-7
 RGT D 7787-70-4 CuBr, E 5961-59-1 Benzenamine,
 4-methoxy-N-methyl-, F 7440-50-8 Cu
 PRO C 647018-70-0
 SOL 71-43-2 Benzene
 CON 6 hours, room temperature
 REFERENCE COUNT: 15 THERE ARE 15 CITED REFERENCES AVAILABLE
 FOR THIS RECORD. ALL CITATIONS AVAILABLE
 IN THE RE FORMAT

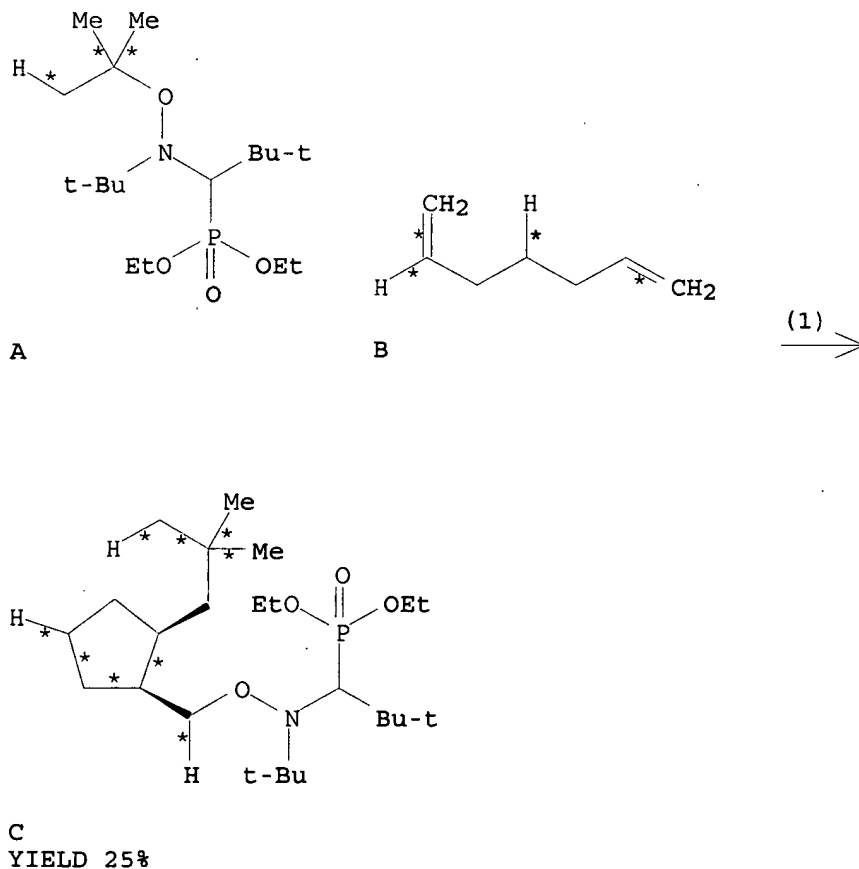
L29 ANSWER 7 OF 8 CASREACT COPYRIGHT 2006 ACS on STN
 ACCESSION NUMBER: 138:368316 CASREACT
 TITLE: Alkoxyamine-Mediated Radical Cyclizations
 AUTHOR(S): Leroi, Corinne; Fenet, Bernard; Couturier,
 Jean-Luc; Guerret, Olivier; Ciufolini, Marco
 A.
 CORPORATE SOURCE: Laboratoire de Synthese et Methodologie
 Organiques CNRS UMR 5078 and Laboratoire de
 Resonance Magnetique Nucleaire, Universite
 Claude Bernard Lyon 1 and Ecole Superieure de
 Chimie, Villeurbanne, 69622, Fr.
 SOURCE: Organic Letters (2003), 5(7), 1079-1081
 CODEN: ORLEF7; ISSN: 1523-7060
 PUBLISHER: American Chemical Society
 DOCUMENT TYPE: Journal
 LANGUAGE: English

GI



AB A new "conjunctive" radical cyclization process that involves the reaction of a 1,6-diene with the Tordo alkoxyamine, an agent originally developed for the radical polymerization of certain olefins through the "persistent radical effect", is developed. For example, thermolysis of non-conjugated dienes I [X = O, CH₂, (EtO₂C)₂C, PhCH₂OCON, 4-BrC₆H₄SO₂N] in the presence of Tordo alkoxyamine gave cycloadducts II [R = (EtO)₂POCH(CMe₃)] predominantly as cis-isomers in 25-51% yields. Acidic cleavage of II [R = (EtO)₂POCH(CMe₃)] afforded the corresponding hydroxylamines II (R = H) in good yields (74-99%).

RX(1) OF 18 A + B ==> C...



RX(1) RCT A 462104-38-7, B 3070-53-9
 PRO C 521276-79-9
 SOL 75-65-0 t-BuOH
 CON 60 hours, 120 deg C
 NTE stereoselective

REFERENCE COUNT: 36 THERE ARE 36 CITED REFERENCES AVAILABLE
 FOR THIS RECORD. ALL CITATIONS AVAILABLE
 IN THE RE FORMAT

L29 ANSWER 8 OF 8 CASREACT COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 133:309685 CASREACT
 TITLE: Method for preparing alkoxyamines from
 nitroxides
 INVENTOR(S): Couturier, Jean-Luc; Guerret, Olivier;
 Senninger, Thierry
 PATENT ASSIGNEE(S): Elf Atochem S. A., Fr.
 SOURCE: PCT Int. Appl., 25 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: French
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

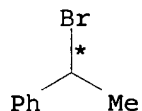
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2000061544	A1	20001019	WO 2000-FR750	20000324
W: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
RW: GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
FR 2791979	A1	20001013	FR 1999-4405	19990408
FR 2791979	B1	20030516		
CA 2334845	AA	20001019	CA 2000-2334845	20000324
BR 2000006023	A	20010313	BR 2000-6023	20000324
EP 1086073	A1	20010328	EP 2000-914251	20000324
EP 1086073	B1	20030312		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI				
JP 2002541239	T2	20021203	JP 2000-610821	20000324
AT 234275	E	20030315	AT 2000-914251	20000324
ES 2193946	T3	20031116	ES 2000-914251	20000324
NO 2000006219	A	20010129	NO 2000-6219	20001207
BG 105035	A	20010731	BG 2000-105035	20001208
US 6495720	B1	20021217	US 2001-719042	20010223
PRIORITY APPLN. INFO.:			FR 1999-4405	19990408
			WO 2000-FR750	20000324

OTHER SOURCE(S): MARPAT 133:309685

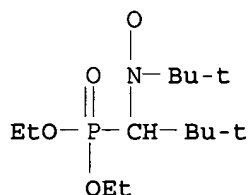
AB The invention concerns a method for preparing alkoxyamines which consists in mixing in an organic solvent, a metallic salt, a metal ligand, a halo-carbon ZX compound, and a nitroxide; in maintaining

the reaction medium stirred at a temperature ranging between 20 >C and 90 >C, until the nitroxide disappears; in recuperating the organic by evaporating the organic solvent under reduced pressure. E.g., reaction of TEMPO with PhCHBrMe in presence of Cu, CuBr and N,N,N',N',N''-pentamethyldiethylenetriamine gave 97% 1-(2,2,6,6-tetramethylpiperidinyloxy)-1-phenylethane.

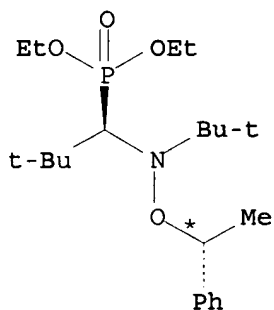
RX(1) OF 3 A + B ==> C



A



B



C
YIELD 99%

RX(1) RCT A 585-71-7, B 188526-94-5

STAGE(1)

CAT 3030-47-5 PMDETA, 7787-70-4 CuBr

SOL 108-88-3 PhMe

STAGE(2)

RGT D 7732-18-5 Water

PRO C 288583-77-7

NTE USING ANOTHER LIGAND GAVE TWO ISOMERS

REFERENCE COUNT:

2

THERE ARE 2 CITED REFERENCES AVAILABLE
FOR THIS RECORD. ALL CITATIONS AVAILABLE
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